

Contents: Chemicals, Working With

Effective Date: May 2004

Point of Contact: Industrial Hygiene Manager

Section

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- 2. Using the Chemical Hygiene Plan in Laboratories (Lab Standard)
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- Obtain an MSDS for all chemicals.
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- Update CMS inventory.
- Dispose and transport chemicals appropriately.

Definitions

Exhibits

Carcinogen Sign

Handbook on Chemical Use in HazCom Operations

Handbook on Chemical Use in Laboratories (Lab Standard)

Highly Acute Toxin Sign

Reproductive Toxin Sign

Forms

None

Training Requirements and Reporting Obligations

This subject area contains training requirements. See the <u>Training and Qualifications</u> Web Site.

This subject area does not contain reporting obligations.

References

29 CFR 1910 OSHA Subpart Z - Toxic and Hazardous Substances

Additional Medical Surveillance (AMS) Form, Occupational Medicine Clinic (OMC) Web Site

Business Systems Division (BSD) Chemical Management System (CMS)

<u>Chemical Management System (CMS)</u> Web Site

CMS Bar Code Label Removal Sheet

CMS Chemical Deletion/Removal Form

CMS Chemical Exchange

CMS Inventory Reports and Queries

CMS Chemical Registration Form

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DOE/BNL Carcinogens Table

Emergency Preparedness Subject Area

Environmental Management System

ES&H Standard 4.10.2, Flammable Liquids: Storage, Use, and Disposal

ES&H Standard 5.1.0, Nonflammable Cryogenic Liquids

Hazardous Waste Management Subject Area

Job Assessment Form (JAF), Occupational Medicine Clinic (OMC) Web Site

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Transportation of Hazardous Materials Off-site Subject Area

<u>Using Controlled Substances in Research</u> Subject Area

What Chemicals Need to Be Inventoried in the CMS

Work Planning and Control for Experiments and Operations Subject Area

*Access limited to BNL staff and authorized non-BNL staff.

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Standards of Periormance

All staff and guests shall comply with applicable Laboratory policies, standards, and procedures, unless a formal variance is obtained.

Managers shall analyze work for hazards, authorize work to proceed, and ensure that work is performed within established controls.

All staff and users shall identify, evaluate, and control hazards in order to ensure that work is conducted safely and in a manner that protects the environment and the public.

All staff and users shall ensure that they are trained and qualified to carry out their assigned responsibilities, and shall inform their supervisor if they are assigned to perform work for which they are not properly trained or qualified.

Management System

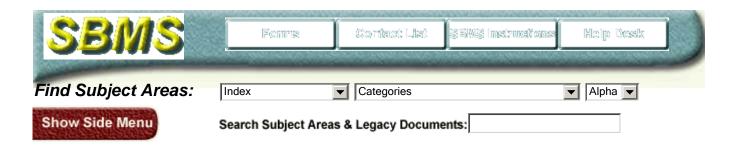
This subject area belongs to the Worker Safety and Health management system.

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Introduction: Chemicals, Working With

Effective Date: May 2004

Point of Contact: Chemical Hygiene Officer

This subject area provides requirements and guidance for all users of chemicals at Brookhaven National Laboratory (BNL). Compliance with these requirements ensures that BNL workers and guests are provided safe workplaces and healthy environments.

This subject area also serves as an essential component of the BNL work planning and control requirements for work involving chemicals. These chemical safety requirements address training, selection, use and handling, storing, transporting (on-site and off-site), and disposal in a manner that meets Laboratory expectations.

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Subject Area: Chemicals, Working With

1. Determining the Applicability of the Hazard Communication Program or the Chemical Hygiene Plan for Laboratories

Effective Date: May 2004

Point of Contact: Industrial Hygiene Manager, ES&H Coordinator

Applicability

This information applies to staff who acquire, manage, use, supervise the use of, store, synthesize, dispose, or transport chemicals.

Occupational Safety and Health Administration (OSHA) has two regulations that govern the use of chemicals in the workplace and require written programs:

- a. 29 CFR 1910.1450, Occupational Exposure to Hazardous Chemicals in Laboratories (Lab Standard); requires a Chemical Hygiene Plan.
- b. 29 CFR 1910.1200, Hazard Communication (HazCom); requires a Hazard Communication Program.

Required Procedure

Step 1	ES&H Coordinators, in conjunction with Line Management Designees, determine if staff work and/or workplace areas fall into one of the following three categories:
	a. No chemical use;
	b. Chemical use according to the Chemical Hygiene Plan for Laboratories;
	c. Chemical use according to the Hazard Communication Program.

Contact the <u>Industrial Hygiene Representative</u> or <u>ES&H Coordinator</u> for assistance with this procedure.

Materials which are exempt include the following:

- Tobacco products, foods, and cosmetics;
- Consumer products used in a manner consistent with typical consumer use (e.g., typing correction fluid, glass cleaner, copier toner, and scouring powder);
- Prescription drugs when used in a manner prescribed by a physician;
- Over-the-counter medications.

Step 2

ES&H Coordinators, in conjunction with Line Management Designees, follow section <u>Using the Chemical Hygiene Plan in Laboratories (Lab Standard)</u> if work areas/ operations meet the following criteria:

- Containers used for chemical reactions, transfers, and other handling of substances are designed to be easily and safely manipulated by one person;
- Multiple chemical procedures or chemicals are used;
- The procedures involve relatively small quantities of hazardous chemicals which are not part of a production process;
- Protective laboratory practices and equipment (e.g., laboratory hoods and lab coats) are effective in minimizing potential employee exposure to hazardous chemicals, available, and in common use.

Step 3

ES&H Coordinators, in conjunction with Line Management Designees, follow section <u>Using the Hazard Communication Plan for Working With Chemicals in HazCom Operations</u> if the use of chemicals does not meet criteria in Step 1 or Step 2. Criteria that apply include the following:

- Chemicals used in the construction or demolition of buildings;
- Workplaces whose function is to produce commercial quantities of material;
- Custodial, maintenance, shops, plumbing, electrical, and trades work areas/operations.
- Large experimental machines.

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Subject Area: Chemicals, Working With

2. Using the Chemical Hygiene Plan in Laboratories (Lab Standard)

Effective Date: May 2004

Point of Contact: Chemical Hygiene Officer

Applicability

This information applies to staff who plan, acquire, manage, use, supervise use of, store, synthesize, dispose, or transport chemicals in laboratories.

Required Procedure

Using the Chemical Hygiene Plan in Laboratories (Lab Standard) contains the following subsections:

- 2.1 Planning to Use Chemicals in Laboratories
- 2.2 Acquiring Chemicals for Laboratories
- 2.3 Using Hazardous Chemicals in Laboratories
- 2.4 Working With OSHA Particularly Hazardous Substances
- 2.5 Synthesizing Chemicals in Laboratories
- 2.6 Storing Chemicals in Laboratories
- 2.7 Disposing Chemicals From Laboratories
- 2.8 Transporting Hazardous Chemicals On-site or Off-site From Laboratories

2.1 Planning to Use Chemicals in Laboratories

Note: Cradle-to-grave management of chemicals must be planned for, including acquisition, use, supervision, storage, and disposal of chemicals.

Contact the <u>Industrial Hygiene Representative</u>, <u>Facility Support Representative</u>, <u>Environmental Compliance Representative (ECR)</u>, or <u>ES&H Coordinator</u> for assistance with this procedure.

Step 1 Review Work Planning and Control documentation to ensure compliance

Area, and the guidelines in exhibit Handbook on Chemical Use in Laboratories. Update the Work Planning and Control documentation when new chemical hazards are introduced. Identify specific chemical needs at the planning stage, including the following:

- Determine whether the chemicals to be used are hazardous, and if so, whether a less hazardous chemical or non-chemical method could be used;
- Determine the hazard of the chemical by reading the <u>Material Safety</u>
 <u>Data Sheet (MSDS)</u>* or contacting the <u>ES&H Coordinator</u>, <u>Industrial</u>
 <u>Hygiene Representative</u>, or <u>Facility Support Representative</u>;
- Consider the amount of chemical to be used or reused, the manner in which the chemical will be used, work location, and if the chemical use is allowed by <u>Facility Use Agreements</u>*;
- Plan to order the smallest quantity of chemical to meet immediate needs. Avoid purchasing more than needed (i.e., to get a volume discount).

Step 2

Plan to perform the task in an area where chemicals can be safely handled. Address and make provisions for the following:

- Compatibility with other operations in the area/building;
- Engineering controls (e.g., ventilation of vapors, fumes, or dust);
- Fire protection concerns;
- Decontamination concerns.

Note: Food preparation and consumption is prohibited in laboratories where chemicals are used or stored.

Plan for the proper storage of chemicals (see subsection <u>Storing Chemicals in Laboratories</u>).

Step 3

Plan for the use of Engineering Controls, Administrative Practices, and Personal Protective Equipment (PPE) (see the <u>Personal Protective</u> <u>Equipment</u> Subject Area) to keep exposures below the specified occupational exposure limits. Contact the <u>ES&H Coordinator</u> for assistance.

Step 4

Determine environmental impact and make provisions for waste minimization, waste disposal, pollution prevention, spill response, and recycling. Consider waste type and disposal cost in the planning of chemical use. Refer to the following resources for guidance:

- Environmental Compliance Representative (ECR) or Waste Management Representative;
- Environmental Management System;
- Chemicals With Special Waste Disposal Concerns exhibit;
- Spill Response Subject Area.

Step 5	Ensure emergency procedures are in place per the Emergency Preparedness and Spill Response Subject Areas. Ensure that emergency equipment (e.g., eye washes, showers, and appropriate PPE) is in place and properly functioning.
Step 6	Supervisor identifies all required training and ensures all personnel complete training prior to performing laboratory work with chemicals. Training to be completed includes the following: • Laboratory Standard Training (HP-IND-220) (see the Training and Qualifications Web Site for course schedule); • Training on additional hazards as needed (e.g., Compressed Gas, Cryogens, Hazardous Waste Generator, Hydrogen Fluoride, etc.). For more information, contact the Department/Division Training Coordinator or see the Training and Qualifications Web Site.
Step 7	Supervisors ensure that employees report to the Occupational Medicine Clinic (OMC) for required medical surveillance, in accordance with regulatory drivers: • Medical surveillance is required when an exposure exceeds regulatory limits for an OSHA-regulated substance; • Medical surveillance may be requested when there is a possibility of exposure above the OSHA regulatory limits. Complete the Job Assessment Form (JAF) before an examination at the OMC. A second form, Additional Medical Surveillance (AMS) Form, is used to request surveillance for those items not on the JAF. These evaluations can be done at the time of the scheduled examination, on request, or at any time. For more information on medical surveillance triggers, see Definition, Criteria, and Additional Information for JAF & AMS. Consult an Industrial Hygiene Representative or Facility Support Representative for an assessment regarding chemical exposures and regulatory exposure levels.
Step 8	If work involves controlled substances (Drug Enforcement Agency [DEA]-regulated substances), follow the <u>Using Controlled Substances in Research</u> Subject Area.

2.2 Acquiring Chemicals for Laboratories

Purchase chemicals through an approved chemical acquisition process: Place a web requisition order. See the Business Systems Division (BSD) Chemical Management System Web page for Chemical Requisition information; • Use an open purchase order if approved for the department in cooperation with CMS; Use a credit card to purchase chemicals only from CMS-approved vendors (see the CMS Vendor Web Pages); Step 1 Place an order with Procurement and Property Management (PPM) Stock. Note: Include all chemicals acquired by any other method (e.g., sponsorprovided chemicals, samples, chemicals from off-site researchers) in the Work Planning and Control process and the CMS inventory (use the Chemical Registration Form). See the What Chemicals Need to Be Inventoried in the CMS for guidance on chemicals that must be entered into the CMS database. After receiving chemicals, check the chemical containers to ensure that they are: Bar-coded with a CMS label, if required; Accounted for under the Static Inventory Designation, or Step 2 • Exempt from CMS. See What Chemicals Need to Be Inventoried in the CMS. If none apply, contact the CMS Team or see the CMS Web Site for additional guidance. The chemical container owner completes the CMS record information regarding the chemical's storage location and user ID (i.e., building number, room number, and Life Number) by: Providing information during the completion of chemical purchase requisition: Step 3 Providing information via a CMS-approved credit card source; Completing and returning information that is provided with any BNL stock chemical purchase: • Completing paper work enclosed with shipping papers when none of the above processes are used; or Notifying the <u>CMS Team</u> if a chemical has not been properly assigned to a location or user. A complete inventory of Material Safety Data Sheet (MSDS) for all chemicals in a laboratory is not required. However, BNL's policy is that MSDS received for laboratory use should be posted in the MSDS* Database. This database serves as the official site for MSDS at BNL and ensures that the most current version is available to BNL employees. If acquiring a chemical whose MSDS is not listed in the BNL MSDS Database, Step 4

- Obtain an MSDS from the manufacturer and send a copy to CMS or,
- Contact CMS for assistance.

For chemicals that are created or molecularly transformed on-site, see subsection <u>Synthesizing Chemicals in Laboratories</u>, regarding the need for the creation of an MSDS.

Guidelines

Staff should check the following resources for availability of chemicals:

- Pollution Prevention Coordinator and other staff;
- CMS Inventory Reports and Queries;
- CMS Chemical Exchange Page.

2.3 Using Hazardous Chemicals in Laboratories

Note: Consuming food or beverages within laboratory chemical-handling areas is prohibited.

Step 1	All staff who work with hazardous chemicals in a laboratory must attend training before they begin work, including: • Laboratory Standard Training (HP-IND-220); • Training on additional hazards as needed (e.g., Compressed Gas, Cryogens, Hazardous Waste Generator, Hydrogen Fluoride, etc.). For more information, contact the Department/Division Training Coordinator or see the Training and Qualifications Web Site.
Step 2	 Personnel without Laboratory Standard Training (HP-IND-220) may enter a laboratory only as one of the following: Trained Hazard Communication worker who performs only HazCom work in laboratory work area (e.g., plumber installing a drain line). All such personnel must comply with Work Planning and Control documentation; Untrained person (e.g., visitor or salesperson) escorted by a Laboratory Standard-trained person who communicates the hazards. Untrained persons may not work with chemicals in the laboratory; Vendor service technician escorted by a BNL Laboratory Standard-trained person who communicates the hazards in the laboratory. Note: Service technician training on specific chemical and health hazards involved in the technician's tasks is the responsibility of the technician's employer.
Step 3	All staff working with hazardous chemicals review the Work Planning and

	Control accumentation (c.g., Experimental Calety Iteview).
Step 4	All staff must know the location of emergency eyewash, safety shower, fire alarm pull-box, telephone, fire extinguisher, and spill control materials before beginning work.
Step 5	Use required PPE as specified in planning documentation and Department/Division procedures. Examples of PPE are gloves, respirators, coveralls, and protective suits. See the exhibit Handbook on Chemical Use in Laboratories or contact an Industrial Hygiene Representative for more information on PPE.
Step 6	Conduct hazardous chemical operations that have the potential for exposure (e.g., reactions, pouring, evaporation, or other vapor, mist, fume, or dust-generating operations) in a functioning laboratory hood, glove box, or other engineering control setting. Follow the guidelines in the exhibit Handbook on Chemical Use in Laboratories: If work with a hazardous chemical occurs outside of a laboratory hood, or when working with OSHA Particularly Hazardous Substances, contact an Industrial Hygiene Representative for a hazard assessment.
Step 7	Workers transferring chemicals into other containers refer to exhibit Handbook on Chemical Use in Laboratories.
Step 8	Supervisors ensure that all personnel receive medical evaluation by the OMC when personnel: • Show signs or symptoms associated with chemical exposure; • Are involved in a chemical spill or leak; • Receive significant exposure from a chemical spill or leak.
Step 9	 When working alone with hazardous chemicals during off hours: Verify that someone else is in the general area and is aware of work with chemical activities and location, or Notify the Safeguards and Security Division at ext. 2238 of location, duration of work, and estimated time of departure. Note: Do not work alone if prohibited by the Supervisor or Work Planning and Control documentation.

Guidelines

All employees handling hazardous chemicals may access information consisting of the symptoms and signs associated with exposures, safe handling, storage, and disposal from the MSDS* Database or by contacting an Industrial Hygiene Representative.

2.4 Working With OSHA Particularly Hazardous Substances

Step 1	Identify chemicals used that are defined by OSHA as <i>Particularly Hazardous Substances</i> . Determine if carcinogens, reproductive hazards, and highly toxic chemicals meet this classification. When using Particularly Hazardous Substances in operations, it is required to utilize additional safety precautions for all chemicals.
Step 2	In the Work Planning and Control documentation, consider the need for: • Establishing a Designated Area and Posting that restricts access to authorized personnel. The Designated Area can be a limited area (e.g., hood, glove box, cabinet) or the entire laboratory. Use exhibits Carcinogen Sign, Reproductive Toxin Sign, Highly Acute Toxic Sign, or equivalent. • Using containment devices (e.g., hood, glove box, or effective exhaust-capturing equipment). All hazardous chemical operations that are not conducted with an engineering control must have a Hazard Assessment reviewed by an Industrial Hygiene Representative. • Establishing work area clean-up and final decontamination procedures. Include procedures for safe removal of contaminated waste. Contact an Industrial Hygiene Representative for guidance on the information that should be incorporated in the Experimental Safety Review document.
Step 3	Supervisors identify applicable hazard-specific training (e.g., Lead, Beryllium, Methylene Chloride) in the Work Planning and Control documentation. Supervisors advise personnel working with OSHA Particularly Hazardous Substances of the special hazard of the chemicals in use prior to assignments involving new exposure situations, as appropriate.
Step 4	When the exposure levels may routinely exceed the action level (or in the absence of an action level, the OSHA Permissible Exposure Limit [PEL]), contact an IH Representative or Facility Support Representative to perform employee exposure monitoring. The Supervisor updates the Work Planning and Control documentation, as necessary.
	Supervisors ensure that employees report to the OMC for required medical

Step 5	surveillance when exposure exceeds regulatory limits or there is a possibility of exceeding OSHA regulatory limits. Complete the Job Assessment Form (JAF) before an examination at the OMC. A second form, Additional Medical Surveillance (AMS) Form, is used to request surveillance for those items not on the JAF. These evaluations can be done at the time of the scheduled examination, on request, or at any time.
	For more information on medical surveillance triggers, see Definition , Criteria , and Additional Information for JAF & AMS.
	Consult an Industrial Hygiene Representative or Facility Support Representative for an assessment regarding chemical exposures and regulatory exposure levels.

2.5 Synthesizing Chemicals in Laboratories

Step 1	 Obtaining a MSDS from another source, if available (i.e., the chemical is available from an off-site manufacturer). See the BNL MSDS Database for guidance on obtaining an MSDS or contact the CMS Team for assistance. If a pre-existing MSDS is not available, evaluate the hazard based on the best available information from similar compounds and literature sources or contact an Industrial Hygiene Representative. Prepare an MSDS if transferring the chemical off-site or to another BNL owner. Contact an Industrial Hygiene Representative for assistance in creating an MSDS. Note: Preparation of an MSDS is not required if the chemical will only be used within the synthesizer's laboratory.
Step 2	If the new chemical introduces a hazard (i.e., toxic, corrosive, fire, or reactive) that did not exist before synthesizing the chemical, update control measures and Work Planning and Control documentation to address the new hazard. Ensure that workers are made aware of changes.

2.6 Storing Chemicals in Laboratories

Step 1	Store chemicals according to the exhibit Handbook on Chemical Use in Laboratories to address flammability, reactivity, compatibility, and spill containment.
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Step 2	 Ensure that the Chemical Management System (CMS) Inventory is consistent with the chemicals stored. Keep the inventory up to date by: Deleting the bar-code number when chemicals are consumed, converted, or disposed; Transferring bar-codes to new owners or locations; Adding bar-codes when chemicals are obtained. Use the forms from the Chemical Management System (CMS) Web Site or contact the CMS Team.
Step 3	Minimize inventory in the following ways: Keep quantities on hand for immediate use; Monitor time-sensitive chemicals for expiration dates; Identify chemicals that no longer serve a purpose and process for disposal (see subsection Disposing of Chemicals From Laboratories).

2.7 Disposing Chemicals From Laboratories

Step 1	Determine the appropriate waste category and follow the appropriate Subject Area: • Sink-Releasable Chemical List from the Liquid Effluents Subject Area; • Hazardous Waste Management Subject Area. Contact the Environmental Compliance Representative, Waste Management Representative, or ES&H Coordinator for assistance.
Step 2	If the chemical container has a CMS bar-code label: Remove the label and enter the bar-code number on the Chemical Deletion/Removal Form, or Remove the label and place the label on a CMS Bar Code Label Removal Sheet. Send the sheet to the CMS Team, Building 120.
Step 3	If the chemical is listed under CMS in a static/revolving inventory: • Enter the bar-code number on the Chemical Deletion/Removal Form or notify the CMS Team. • The CMS team will update and send the chemical owner a new static posting form. • The chemical owner replaces the existing posting form with the revised form.

Guidelines

Some wastes are very difficult to dispose of due to chemical contents or mixtures of chemicals. The Waste Management Division (WMD) recommends keeping the following chemicals segregated from other hazardous constituents:

- Mercury;
- Polychlorinated biphenyls (PCB);
- Asbestos.

Due to nationwide restrictions, the WMD recommends as much advanced notice as possible when disposing of the following chemicals:

- Arsenic trioxide, unused;
- Mercurous fluoride;
- Pentachlorophenol and its mixtures.

2.8 Transporting Hazardous Chemicals On-site or Off-site From Laboratories

Step 1	Before transporting hazardous non-radioactive chemicals for transfer on- site, ensure that they are appropriately packaged and meet all requirements specified in the <u>Transfer of Hazardous Materials On-site</u> Subject Area.
Step 2	Before shipping hazardous non-radioactive chemicals to off-site locations or allowing a researcher to bring chemicals to BNL, ensure that chemicals are appropriately packaged and meet all requirements specified in the Transportation of Hazardous Materials Off-site Subject Area.
Step 3	See the section <u>Packaging and Transferring Radioactive Material On-site</u> in the <u>Transfer of Radioactive Materials On-site</u> Subject Area for regulations for transferring radioactive materials on-site.

References

Additional Medical Surveillance (AMS) Form, Occupational Medicine Clinic (OMC) Web Site

Business Systems Division (BSD) Chemical Management System

Chemical Management System (CMS) Web Site

Chemical Registration Form

CMS Bar Code Label Removal Sheet

CMS Chemical Deletion/Removal Form

CMS Chemical Exchange

CMS Inventory Reports and Queries

CMS Vendor Web Pages

<u>Definition, Criteria, and Additional Information for JAF & AMS, Occupational Medicine Clinic</u> (OMC) Web Site

Emergency Preparedness Subject Area

Environmental Management System

Hazardous Waste Management Subject Area

Job Assessment Form (JAF), Occupational Medicine Clinic (OMC) Web Site

Material Safety Data Sheet (MSDS)*

Liquid Effluents Subject Area

Spill Response Subject Area

Training and Qualifications Web Site

Transfer of Hazardous Materials On-site Subject Area

Transfer of Radioactive Materials On-site Subject Area

Transportation of Hazardous Materials Off-site Subject Area

Using Controlled Substances in Research Subject Area

What Chemicals Need to Be Inventoried in the CMS

Work Planning and Control for Experiments and Operations Subject Area

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Subject Area: Chemicals, Working With

3. Using the Hazard Communication Plan for Working With Chemicals in HazCom Operations

Effective Date: May 2004

Point of Contact: Chemical Hygiene Officer

Applicability

This information applies to personnel who plan, acquire, manage, use, supervise use of, store, synthesize, dispose of, or transport chemicals in non-laboratory operations (e.g., shops, manufacturing, maintenance, custodial activities, construction, and large experimental machines).

Required Procedure

Using the Hazard Communication Plan for Working With Chemicals in HazCom Operations contains these subsections:

- 3.1 Planning to Use Chemicals for HazCom Operations
- 3.2 Acquiring Chemicals for HazCom Operations
- 3.3 Using Hazardous Chemicals in HazCom Operations
- 3.4 Storing Chemicals for HazCom Operations
- 3.5 Disposing of Chemicals From HazCom Operations
- 3.6 Transporting Hazardous Chemicals Onsite or Offsite for HazCom Operations

3.1 Planning to Use Chemicals for HazCom Operations

Cradle-to-grave management of chemicals must be planned for, including the acquisition, use, storage, transporting, and disposal of chemicals.

Contact an <u>Industrial Hygiene Representative</u>, <u>Facility Support Representative</u>, <u>Environmental Compliance Representative (ECR)</u>, or <u>ES&H Coordinator</u> for assistance with this procedure.

Step 1 | Supervisors identify chemical needs and determine whether the chemical is

hazardous, and if so, whether a less hazardous chemical or non-chemical method could be used. **Note:** If you are not sure of the hazard of the chemical, read the <u>Material Safety Data Sheet (MSDS)</u>* or contact your <u>ES&H Coordinator</u>, <u>Industrial Hygiene Representative</u>, or <u>Facility Support Representative</u>.

- Use on-site chemicals when possible via the <u>Chemical Management System (CMS) Chemical Exchange</u>.
- Plan to order the smallest quantity of chemical to meet immediate needs.
- Plan for the storage of chemicals.
- Consider waste type and disposal cost in the planning of chemical use.
 Contact an ECR or Waste Management Representative for assistance.

Note: Mixed waste (radiological and hazardous) incurs considerable expense.

- Step 2 Complete new or update existing Work Planning and Control documentation.

 Ensure planned operations comply with the guidelines in exhibit Handbook on Chemical Use in HazCom Operations.
- Plan mechanisms to maintain employee exposures below the specified occupational exposure limits by using Engineering Controls, Administrative Practices, and Personal Protective Equipment (PPE). Contact your ES&H Coordinator for assistance.
- **Step 4** Consider actions to be taken regarding future waste handling and disposal (see subsection <u>Disposing of Chemicals From HazCom Operations</u>).
- Step 5 Determine environmental impact and make provisions for waste minimization, waste disposal, pollution prevention, spill response, and recycling. Consider waste type and disposal cost in the planning of chemical use. Refer to the following resources for assistance:
 - Your ECR and Waste Management Representative;
 - Environmental Management System;
 - Spill Response Subject Area.
- **Step 6** Before acquiring chemicals, ensure the following:
 - Adequate storage facilities are available. For assistance, contact the Building Manager and ES&H Coordinator.
 - Appropriate spill response materials are available (see the <u>Spill Response</u> Subject Area).

Guidelines

Examples of controls to minimize worker exposure to hazardous chemicals (and the order they should be used) are:

- Substitution with less hazardous chemicals;
- Engineering controls (mechanical equipment that reduces employee exposure by removing contaminants from the work area. Examples are lab hoods, "smoke-eaters," "elephant trunk" exhausts, and other types of exhaust fans);
- Administrative controls (rules, work practices, and other supervisory means). Examples
 of administrative controls are:
 - Signs and postings to prevent access to hazard areas without appropriate training and PPE;
 - Training requirements;
 - Reducing the time of worker exposure includes:
 - dividing a job into smaller parts that several workers can work on to reduce the exposure to any one person;
 - dividing a job into smaller parts and completing the work over several days to reduce the exposure to the worker on any one day;
 - conducting "dry run" practices to discover technique problems and gain experience.
- PPE (e.g., gloves, respirators, lab coats, coveralls, and protective suits) should be used only:
 - When engineering and administrative controls are not sufficient to control exposure:
 - While engineering controls are being installed;
 - When engineering and administrative controls are not possible.

3.2 Acquiring Chemicals for HazCom Operations

Chemicals must be accounted for in the Chemical Management System (CMS). See What Chemicals Need to Be Inventoried in CMS for guidance.

Step 1	 Purchase chemicals through an approved chemical acquisition process: Place a web requisition order. See the <u>Business Systems Division (BSD) Chemical Management System</u> Web page for Chemical Requisition information; Use an open purchase order if approved for your department in cooperation with CMS; Use a credit card to purchase chemicals only from CMS-approved vendors (see the <u>CMS Vendor Web Pages</u>); Place an order with Procurement and Property Management (PPM) Stock.
Step 2	Ensure chemicals acquired by any other method (e.g., sponsor-provided chemicals, samples, chemicals from offsite researchers) are included in the Work Planning and Control process and the CMS.

Step 3	Before a chemical is brought into the facility, determine if it introduces a new hazard. If the hazard is not covered in Work Planning and Control or internal process documentation, notify the ES&H Coordinator , IH Representative , or Facility Support Representative .	
Step 4	Ensure acquired chemicals meet the labeling guidelines in the exhibit Handbook on Chemical Use in HazCom Operations.	
Step 5	After receiving chemicals, check the chemical containers to ensure that they are: • bar-coded with a CMS label, if required; • accounted for under the CMS Static Inventory Designation, or • exempt from CMS (see What Chemicals Need to Be Inventoried in CMS). If none apply, contact the CMS Team or see the CMS Web Site for additional guidance.	
Step 6	 The chemical container owner completes the CMS record information regarding the chemical's storage location and user ID (i.e., building number, room number, and Life Number) by: Providing information during the completion of chemical purchase requisition; Providing information via a CMS-approved credit card source; Completing and returning information that is provided with any BNL stock chemical purchase; Completing paper work enclosed with shipping papers when none of the above processes are used, or; Notifying the CMS Team when it is known that a chemical has not been properly assigned to a location or user. 	
Step 7	If you acquire a chemical whose Material Safety Data Sheet (MSDS) is not listed in the BNL MSDS Database: • Obtain an MSDS from the manufacturer and send a copy to CMS or • Contact CMS for assistance.	
	 The chemical owner obtains an MSDS when an MSDS is not available for the following: A new, unique chemical from the reaction of two or more chemicals; A mixture of existing chemicals that presents a new hazard not covered by the MSDS for the components; A chemical created or molecularly transformed onsite. 	

Step 8

Note: A new MSDS does not need to be created for dilutions or reacted products such as paint, epoxies, or glues.

Obtain an MSDS for the chemical from another source, if available from an offsite manufacturer. See the BNL MSDS* Database for guidance on obtaining an MSDS, or contact the CMS Team for assistance in finding an MSDS.

If a pre-existing MSDS cannot be obtained, have a MSDS prepared for BNL users and offsite users. Contact an <u>Industrial Hygiene Representative</u> for assistance in creating an MSDS.

If the new chemical introduces a type of hazard (toxic, corrosive, fire, or reactive) that did not exist before, update training, control measures, and planning documentation to address the new hazard.

Guidelines

Staff should check the following resources for availability of chemicals:

- Pollution Prevention Coordinator and other staff;
- CMS Inventory Reports and Queries;
- CMS Chemical Exchange Page.

3.3 Using Hazardous Chemicals in HazCom Operations

Step 1	 All staff working with hazardous chemicals (i.e., hazcom employees) must do the following: Receive training about the chemicals in their workplace before beginning work. For more information, contact the Department/Division Training Coordinator or see the Training and Qualifications Web Site. Understand the hazards of chemicals used from the Work Planning and Control documentation and MSDS. Contact the Supervisor or Industrial Hygiene Representative for concerns or questions. Know the location of emergency eyewash, safety shower, fire alarm pull-box, telephone, and fire extinguisher, and how to use appropriate spill control materials before beginning work.
	When working alone with hazardous chemicals during off hours: • Verify that someone else is in your general area and is aware of your work with chemical activities and your location, so they may periodically check on you, or

Step 2 Notify the Safeguards and Security Division at ext. 2238 of your location, duration of work, and when you leave the area, so they may periodically check on you. Note: Do not work alone if prohibited by your Supervisor or the Work Planning and Control documentation. Follow the exposure control and exposure monitoring processes outlined in the Work Planning and Control or skill-of-the-craft documents. Use required Personal Protective Equipment (PPE) as specified in planning documentation and Department/Division procedures. Examples of PPE are gloves, respirators, coveralls, and protective suits. For more information, Step 3 consult the following: Handbook on Chemical Use in HazCom Operations exhibit; Personal Protective Equipment (PPE) Subject Area; Industrial Hygiene Representative. When working with an OSHA Regulated Chemical (see **DOE/BNL** Carcinogens Table), the Supervisor contacts an Industrial Hygiene Representative for a hazard assessment and guidance on additional safety precautions above the safe handling procedures for all chemicals. When the exposure levels may routinely exceed the action level (or in the absence of an action level, the OSHA Permissible Exposure Limit [PEL]), for an OSHA Regulated Chemical: • Contact an Industrial Hygiene Representative or Facility Support Step 4 Representative to perform employee exposure monitoring; Prepare an Exposure Control Plan for operations that exceed the OSHA PEL; the plan documents engineering and administrative controls and PPE to be used. Supervisors identify applicable hazard-specific training (e.g., Lead, Beryllium, Methylene Chloride) in the Work Planning and Control documentation. Supervisors advise personnel working with OSHA Regulated Chemicals of the special hazard of the chemicals in use prior to assignments involving new exposure situations, as appropriate. Supervisors ensure that all personnel receive medical evaluation by the Occupational Medicine Clinic (OMC), when workers are: Exposed above Occupational Exposure Limits; Step 5 Show signs or symptoms associated with a chemical exposure; Involved in a significant chemical spill or leak; Involved in a chemical explosion; Work with an OSHA Regulated Chemical (see DOE/BNL Carcinogens Table). Use engineering controls and work techniques that minimize generation of Step 6 dust, fumes, mists, and vapors into the work area. Conduct hazardous onaratione lieina an avhallet evetam whan nacaeearv

	operations using an exhaust system when hecessary.	
Step 7	Maintain labels on containers according to the exhibit Handbook on Chemical Use in HazCom Operations. OSHA Select Carcinogens or ACGIH Carcinogens must be labeled with a carcinogen warning and staff must be informed that the chemical is a potential carcinogen.	
Step 8	The chemical container owner follows the Chemical Management System (CMS) guidance in the Handbook on Chemical Use in HazCom Operations exhibit, including notifying the CMS Team of any of the following: • If the chemical's owner (designated CMS Contact Person) changes; • If the chemical's storage location (i.e., building number, room number, and the location within the room) changes; • If chemicals are consumed or disposed of (see subsection Disposing of Chemicals From HazCom Operations).	
Step 9	When working in HazCom areas, do not consume food and beverages.	

Guidelines

- All employees handling Hazardous Chemicals may access information consisting of the symptoms and signs of exposure, safe handling, storage, and disposal from the <u>Chemical Management System (CMS)</u> Web Site or by contacting the <u>Industrial Hygiene</u> <u>Group</u>.
- The OSHA Regulated Carcinogens Exposure Control Plan needs to address the following:
 - Signs and labels to warn about the hazards associated with these carcinogens;
 - Medical surveillance for employees assigned to enter regulated carcinogen areas;
 - Initial monitoring if there is reason to believe that exposure levels for the carcinogen routinely exceed the action level (or in the absence of an action level, the PEL);
 - Periodic monitoring: If the initial monitoring discloses exposure over the action level (or in the absence of an action level, the PEL), exposure monitoring consistent with the OSHA standard must be implemented;
 - Establishment of a limited-access, regulated carcinogen area, which is a fully enclosed structure that prevents the entry of the carcinogen into non-regulated areas or the external environment. Access restricted to authorized personnel only;
 - Use of containment devices, such as fume hoods or glove boxes, and/or appropriate PPE (e.g., respirators, protective clothing);
 - Requirement for staff working with OSHA Regulated Carcinogens to wash their hands, forearms, face, and neck upon exiting from the regulated area, close to the point of exit, and before engaging in other activities;
 - Availability of a clean change room where clean clothing and/or PPE can be donned in an environment free of the OSHA Regulated Carcinogens. This change room must be adjacent to and have an entry from a shower room, when required;
 - Procedures for safe removal of contaminated waste;
 - Decontamination procedures.

3.4 Storing Chemicals for HazCom Operations

Step 1	Store chemicals according to the exhibit Handbook on Chemical Use in HazCom Operations to address flammability, reactivity, compatibility, and secondary containment.
Step 2	 Ensure that the Chemical Management System (CMS) inventory is consistent with the chemicals stored. Keep the following up to date: Deleting the bar-code number when chemicals are consumed, converted, or disposed; Transferring bar-code to new owners or locations; Adding bar-codes when chemicals are obtained. Contact the CMS Team or use the forms from the CMS Web Site.
Step 3	 Minimize inventory, including the following: Keep quantities on hand to quantity needed for immediate use; Monitor time-sensitive chemicals for expiration dates; Identify chemicals that no longer serve a purpose and process for disposal (see subsection <u>Disposing of Chemicals From HazCom Operations</u>).

Guidelines

Additional reference material on the hazards, safe handling, storage and disposal of chemicals can be obtained from the <u>CMS</u> Web Site or by contacting the <u>Industrial Hygiene</u> <u>Group</u>.

3.5 Disposing of Chemicals From HazCom Operations

	Determine the appropriate waste category and follow the appropriate Subject Area:
Step 1	 Sink-Releasable Chemical List from the Liquid Effluents Subject Area Hazardous Waste Management Subject Area
	Contact your Environmental Compliance Representative, Waste Management Representative, or ES&H Coordinator for assistance.
	If the chemical container has a CMS bar-code label:

Step 2	 Remove the label and enter the bar-code number on the <u>CMS</u> <u>Chemical Deletion/Removal Form</u>, or Remove the label and place the label on a <u>CMS Bar Code Label</u> <u>Removal Sheet</u>. Send the sheet to the CMS Team, Building 120.
Step 3	If the chemical is listed under CMS in a static/revolving inventory: • Enter the bar-code number on the Chemical Deletion/Removal Form or notify the CMS Team. • The CMS team will update and send the chemical owner a new static posting form. • The chemical owner replaces the existing posting form with the revised form.

Guidelines

Some wastes are very difficult to dispose of due to chemical contents or mixtures of chemicals. The Waste Management Division (WMD) recommends keeping the following chemicals segregated from other hazardous constituents:

- Mercury;
- Polychlorinated biphenyls (PCB);
- Asbestos.

Due to nationwide restrictions, the WMD recommends as much advanced notice as possible when disposing of the following chemicals:

- Arsenic trioxide, unused;
- Mercurous fluoride:
- Pentachlorophenol and its mixtures, typically wood preservative.

3.6 Transporting Hazardous Chemicals Onsite or Offsite for HazCom Operations

Step 1	Before packaging hazardous non-radioactive chemicals and Materials of Trade (MOT) for transfer onsite, ensure that they are appropriately packaged and meet all requirements specified in the Transfer of Hazardous Materials On-site Subject Area.
Step 2	Before shipping hazardous non-radioactive chemicals and Materials of Trade (MOT) for transportation to offsite locations, ensure that they are appropriately packaged and meet all requirements specified in the Transportation of Hazardous Materials Off-site Subject Area.
Step 3	See the section Packaging and Transferring Radioactive Material On-site in the Transfer of Radioactive Materials On-site Subject Area for regulations for transferring radioactive materials onsite.

References

Business Systems Division (BSD) Chemical Management System (CMS)

Chemical Management System (CMS) Web Site

CMS Bar Code Label Removal Sheet

CMS Chemical Deletion/Removal Form

CMS Chemical Exchange

CMS Inventory Reports and Queries

CMS Vendor Web Pages

<u>Definitions, Criteria, and Additional Information for JAF & AMS, Occupational Medicine Clinic</u> (OMC) Web Site

DOE/BNL Carcinogens Table

Emergency Preparedness Subject Area

Environmental Management System

Material Safety Data Sheet (MSDS)*

Personal Protective Equipment (PPE) Subject Area

Spill Response Subject Area

Training and Qualifications Web Site

Transfer of Hazardous Materials Onsite Subject Area

Transfer of Radioactive Materials Onsite Subject Area

Transportation of Hazardous Materials Offsite Subject Area

What Chemicals Need to Be Inventoried in CMS

Work Planning and Control for Experiments and Operations Subject Area

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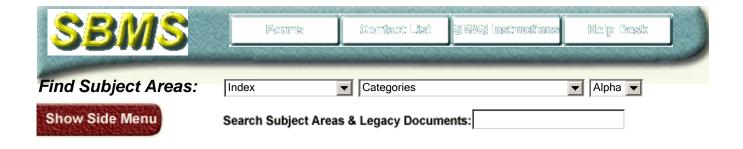
^{*}Access limited to BNL staff and authorized non-BNL staff.

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Definitions: Chemicals, Working With

Effective Date: May 2004

Point of Contact: Industrial Hygiene Manager

Term	Definition
administrative controls	Methods of minimizing inhalation and physical contact exposures through measures such as: Periods away from contaminant or physical stressor through job rotation, limitation of exposure time, or work/rest regimens; Laboratory safety and health procedures; Signs and postings.
chemical	Any element, chemical compound, or mixture of elements and/or compounds.
Chemical Hygiene Officer	An employee who is designated by BNL to provide technical guidance in the development and implementation of the Chemical Hygiene Plan and the Hazard Communication Program. BNL Chemical Hygiene Officer is the Chemical Safety Subject Matter Expert (SME).
Chemical Hygiene Plan	A written program developed and implemented by BNL to set forth procedure, equipment, and work practices that protect employees from the health and safety hazards presented by hazardous chemicals in laboratory settings.
Chemical Management System (CMS)	BNL's chemical management system that enables retrieval of MSDS, chemical forms, location of chemicals and chemical contact persons, communication with the CMS team, and other information on chemicals and chemical resources.
CMS chemical owner	Person who is documented in the CMS system as being responsible for the chemical.
engineering controls	Methods of controlling exposures by eliminating or reducing the presence of the chemical. It includes measures such as: • Substituting a less hazardous chemical;

	 Isolating or enclosing a process or work operation (e.g., use of a closed system, glove box, or toxic gas cabinet); Using wet methods to reduce aerosol generation; Using local exhaust ventilation at the point of generation or laboratory fume hood.
exposure	Contact with a chemical, biological, radiological, or physical hazard. Exposures may be acute (large doses over a short period) or chronic (small doses over a long period).
Hazard Communication Program	A written document that describes BNL's implementation of the OSHA Hazard Communication Standard. The Plan consists of Section Using the Hazard Communication Plan for Working With Chemicals in HazCom Operations of this Subject Area and the exhibit Handbook on Chemical Use in HazCom Operations.
hazardous chemical	Any chemical that poses a physical or health hazard when: • Statistically significant evidence based on at least one study conducted in accordance with established scientific principles shows that acute or chronic health effects may occur in exposed employees; • Scientifically valid evidence shows that the chemical is: • a combustible liquid; • a compressed gas; • explosive; • flammable; • an organic peroxide; • an oxidizer; • pyrophoric; • unstable (reactive); • water-reactive.
hazcom area	Any area where an employee may be exposed to chemicals under normal conditions of use or in a foreseeable emergency, except in areas where there is laboratory use of chemicals, covered under laboratory standard area.
hazcom employee	A worker who may be exposed to hazardous chemicals under normal working/operating conditions or in foreseeable emergencies. Office workers who encounter hazardous chemicals only in nonroutine isolated instances are not hazcom employees.

	Homoutine, isolated mistarioes are not hazeom employees.
health hazard	Any substance that may cause acute or chronic health effects in exposed individuals. Such substances include the following: Carcinogens; Toxic or acutely toxic agents; Reproductive or developmental toxins; Irritants; Corrosives; Sensitizers; Liver, kidney, and nervous system toxins; Agents that act on the blood-forming systems; Agents that damage the lungs, skin, eyes, or mucous membranes; Biologically produced chemical agents.
highly toxic chemical	To be classified as "highly toxic," a chemical must meet the following criteria: • Oral LD-50 in white rats equal to or less than 50 mg/kg; • Dermal LD-50 in white rabbits equal to or less than 200 mg/kg; or • Inhalation LC-50 in white rats equal to or less than 200 ppm (for gases or vapors) or 2 mg/L (for dusts, fumes or mists).
laboratory standard operation	 Laboratory use of chemicals which meets the following conditions: Chemical manipulations are easily carried out by one person; Multiple chemical procedures or chemicals are used; The procedures involved are not part of a production process, nor in any way simulate a production process; Protective laboratory practices and equipment are available and in common use to minimize the potential for employee exposure to hazardous chemicals.
Material Safety Data Sheet (MSDS)	Written or printed materials, supplied by the manufacturer or BNL, containing information on chemical identity, physical and chemical properties, physical hazards, health hazards, protective safety methods, and emergency procedures.
Materials of Trade (MOT)	Certain hazardous materials (e.g., hazardous chemicals or other hazardous material that will be consumed by a staff member's work), when used in direct support of BNL's business, may be transferred from one location to another by a staff member for his or her own use as Materials of Trade (MOT). The regulations for transporting MOT are less restrictive and based on a quantity limit for specific Department of Transportation hazard classes. The BNL Materials of Trade (MOT) exhibit in the Transportation of Hazardous Materials Offsite Subject Area provides the quantity limits for MOT

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NFPA Fire Diamond Label	A labeling system that provides information on health, fire, reactivity, and other hazards associated with the chemical.	
OSHA Regulated Chemicals	Chemicals for which OSHA has promulgated specific regulations in 29 CFR 1910 or 29 CFR 1926.	
OSHA Select Carcinogen	See carcinogen.	
Particularly Hazardous Substance	 A chemical with one or more of the following designations: Carcinogen; Reproductive toxin (see the <u>CMS Reproductive Toxins Table</u>); Substance with a high degree of acute toxicity (see the <u>CMS Highly Acute Toxin Table</u>). 	
Personal Protective Equipment (PPE)	A control measure that places a barrier between the worker and the hazards, and is used when engineering and administrative controls are not sufficient to control exposure; while engineering controls are being installed; and when engineering and administrative controls are not possible. Examples of PPE are gloves, respirators, lab coats, coveralls, and protective suits.	
secondary container	Any container into which chemicals are transferred.	
Secondary containment	Trays or outer jacketing surrounding a container used to minimize or contain a spill if the container breaks or leaks.	

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Subject Area: Chemicals, Working With

Carcinogen Sign

Effective Date: December 2002

Point of Contact: Safety & Health Services Division Manager

The Carcinogen Sign is provided as a PDF file.

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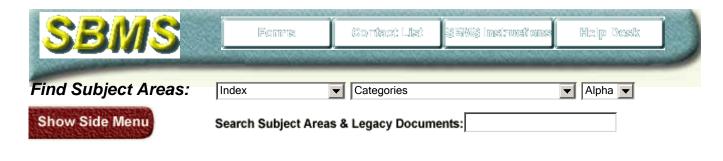
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Carcinogen Designated Area

Authorized Personnel Only

2.0/1716e011.pdf (04/2002)



Subject Area: Chemicals, Working With

Handbook on Chemical Use for Hazcom Operations

Effective Date: May 2004

Point of Contact: Industrial Hygiene Manager

The Handbook on Chemical Use for Hazcom Operations is available as a PDF file.

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BROOKHAVEN

Brookhaven National Laboratory

Handbook on

Chemical Use in HazCom Operations



(OSHA Hazard Communication Standard)

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General Rules for HazCom Use of Chemicals

1. Conduct operations involving hazardous chemicals with engineering control settings in place. Do not conduct operations on open benches. Examples of these types of operations are reactions, pouring, evaporation, or other vapor, mist, fume, or dust-generating operations.



- Limit work with hazardous chemicals on work benches to operations such as opening packing boxes, preparing labels for containers, handling closed containers of chemicals, and preparing non-hazardous test media or equipment (i.e., operations that do not have the potential to result in employee exposure to hazardous levels of chemicals).
- 3. Keep exhaust hoods free of excessive equipment and chemical storage containers.
 - ?? Handle chemicals at least 6 inches into the hood.
 - ?? Keep equipment, boxes, and bottles at least 6 inches from the front face of the hood. Do not obstruct the flow of air into the slot in the rear of the hood.
 - ?? Chemicals that do not restrict the airflow within the hood may be stored within the hood on elevated shelves or platforms (noncombustible material).



- ?? Do not insert your head into the hood when hazardous operations are conducted. Insert only appropriately protected hands and arms into hoods.
- ?? Lower the sash to protect the eyes from a direct path to hazardous operations where splashes or impact could occur. Do not open "sash hoods" beyond the point indicated on the "face velocity test" sticker when conducting hazardous operations.
- ?? Have your lab hood tested for "face velocity" annually.
- **4.** Vent ovens, autoclaves, and other equipment if the process causes hazardous levels of contaminants to be produced within the occupied space.
- **5.** Do not bring or consume food and beverages in chemical-handling areas. Do not store food in chemicals refrigerators. Do not store chemicals in break room and kitchen refrigerators.
- **6.** Do not store bottles of corrosive chemicals (e.g., acids and bases) above eye level.
- 7. Use appropriate Personal Protective Equipment (PPE) to prevent contact with eyes and skin, ingestion, and inhalation. See the SBMS Personal Protective Equipment Subject Area.

Container Labeling in HazCom Operations

Do not remove or deface labels on containers (e.g., bottles, boxes, bags, drums) received from manufacturers and distributors unless they are replaced with a label that contains equivalent wording on the contents.

Manufacturer's label



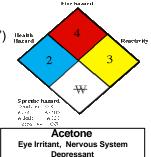
Label stationary containers (e.g., tanks, vessels) with a label that identifies the name of the chemical within the vessel and the hazard of the chemical (i.e., toxicity, fire hazard, reactivity, stability).



When processes require the transfer of all or a portion of a chemical to a new container, <u>identify the chemical name</u> on the new container and the hazard of the chemical (toxicity, fire hazard, reactivity, stability), and the target organ.



The NFPA diamond may be used to convey the hazard on vessels and bottles, but OSHA requires supplementing the rating numbers with the body's "target organ" (such as "burns eyes and lungs" and "toxic to kidney") Illustration on the label.



5. Alternative Means of Labeling: Using codes or numbers on bottles or vessels as a means of labeling is permitted. There must be a logbook, record, sample sheet, or other written record of the codes or numbers that allow all users to know the contents of the container.

All workers in the area need to be familiar with the numbering technique so they can identify the

For example: A bottle could be labeled with "Log: 6-123" if that links to the sixth log book, that notebook was numbered "Log 6," and on page 123 of that notebook the information on the chemical would be found.

Log 6-123

- **6. Temporary Use Containers:** When a container (e.g., bucket, bottle, or beaker) is filled for temporary use, it does not have to be labeled if all the following apply:
 - ?? It will be used only by the person who has filled the temporary container;
 - ?? There is no possibility for misidentification with other containers;
 - ?? It will be not used beyond one shift;
 - ?? It will not be left unattended in an area where other persons are located.



7. Secondary Containment: Use a tray to surround a bottle or vessel to contain the hazardous liquids in the event of a spill or leak. This tray is referred to as secondary containment. Do not label the secondary containment unless it prevents the viewing of the label on the primary vessel.



8. Carcinogens must be labeled with warning that the chemical is a potential carcinogen. Examples of appropriate labels/signs are:







MSDS Availability in HazCom Operations

- 1. BNL maintains the Chemical Management System (CMS) with Material Safety Data Sheet (MSDS) records of chemicals received from manufacturers for HazCom use. The on-line MSDS database is the official method of accessing MSDS information a BNL. The only official copies of MSDS recognized by BNL are those available from the Chemical Management System (CMS). This web-based system ensures that the most current version of an MSDS is available to BNL employees.
- 2. Hard copies of MSDSs are kept in a central location (CMS/MSDS Team Office) for times when the on-line system is not available (i.e., loss of site power or network malfunction). Contact x-6387, x-2028, or CMS Team for an MSDS when the database is not functional.



- 3. A complete inventory of MSDSs for all chemicals in HazCom operations is required. Workers are expected to review the MSDS to learn the hazards of chemicals they work with, especially new chemicals introduced into the area.
- 4. Line organizations may choose to keep hard copies of MSDSs available for employee access, especially in remote areas or areas without computer access. These copies of the MSDSs are not the official BNL version and are to be kept as a supplement or back-up to the CMS system. If this option is used by an organization, the organization is responsible to ensure that hard copies are current and cover the most recent information for the chemical being used.

Terms Frequently Found in MSDS

action level	A chemical concentration designated in an OSHA standard for a specific substance. The action level initiates certain required activities such as exposure monitoring and medical surveillance.
carcinogen	A chemical substance used in the workplace that has been designated as a carcinogen or potential carcinogen in the following sources: ?? National Toxicology Program (NTP), Annual Report on Carcinogens (Known or Reasonably Anticipated); ?? International Agency for Research on Cancer (IARC), Monographs (Group 1A, 2A & 2B); ?? OSHA Standard 29 CFR 1910, Subpart Z, Toxic and Hazardous Substances cited as carcinogens; and ?? American Conference of Governmental Industrial Hygienists (ACGIH), Threshold Limit Values for Chemical Substances and Physical Agents (Appendix A, Categories A1 and A2).
combustible liquid	A liquid having a flash point at or above 100°F (37.8°C). Combustible chemical liquids are subdivided as follows: ?Class II liquids include those having flash points at or above 37.8°C (100°F) and below 60°C

	(140°F).
	?'Class IIIA liquids include those having flash points at or above 60°C (140°F) and below 93°C (200°F). ?'Class IIIB liquids include those having flash points at or above 93°C (200°F).
compressed gas	Any mixture of gases in container with an absolute pressure exceeding 40 psi at 70°F or 104 psi at 130°F, or a liquid having a vapor pressure exceeding 40 psi at 100°F.
corrosive	A material that causes destruction or alteration of human tissue at the site of contact.
cryogenic liquid	A refrigerated liquefied gas having a boiling point colder than -90°C (-130°F) at 101.3pKa (14.7 psi) absolute.
explosives	Chemicals that cause a sudden, almost instantaneous release of pressure, gas, and heat when subjected to sudden shock, pressure, or high temperature.
flammable gas	A gas that is flammable in a mixture of 13% or less (by volume) with air, or the flammable range with air is wider than 2% regardless of the lower limit.
flammable liquid	A liquid having a flash point below 100°F (37.8°C) and having a vapor pressure not exceeding 40 lb. per sq. in. (absolute) (2068 mm Hg) at 100°F (37.8°C). Class I liquids are subdivided as follows: ?Class IA includes those having flash points below 73°F (22.8°C) and having a boiling point below 100°F (37.8°C). ?Class IB includes those having flash points below 73°F (22.8°C) and having a boiling point below 100°F (37.8°C). ?Class IC includes those having flash points below 73°F (22.8°C) and below 100°F (37.8°C).
flammable solid	A substance that is: ?Thermally unstable and can undergo a strongly exothermic decomposition even without participation of oxygen; ?Readily combustible and can cause a fire through friction, such as matches; ?Any material with a burning rate faster than 2.2 mm (0.087 in) per second; ?Any metal powder that can be ignited and react over the whole length of a sample in 10 minutes or less.
irritant	Chemical that has a reversible inflammatory effect on living tissue.
organic peroxide	Compounds that release oxygen readily and are capable of violent or explosive decomposition when exposed to air.
oxidizer	A material that initiates or promotes combustion in other materials, thereby causing fire either of itself or through the release of oxygen or other gases.
permissible exposure limits (PELs)	Airborne concentrations of substances that represent conditions under which it is believed nearly all workers may be repeatedly exposed, daily, without adverse effects. PELs represent time-weighted average concentrations, usually expressed in units of mg/m³ or parts per million (ppm) for an 8-hour workday within a 40-hour work week.
physical hazard	Any chemical that is combustible, explosive, flammable, pyrophoric, unstable (reactive), water reactive, a compressed gas, an organic peroxide, or an oxidizer.

pyrophoric	A chemical that will ignite spontaneously in the ambient atmosphere at or below 130°F.
reproductive toxin	Agents that affect the chromosomal structure of a cell or will adversely affect the developing fetus.
short-term exposure limit® (STEL®)	Amount of a chemical you can safely be exposed to over a 15-minute period.
target organ toxin	Chemical that adversely affects a particular organ in the body.
threshold limit value® (TLV®)	A time-weighted average airborne concentration for a normal 8-hour work day and 40-hour workweek to which nearly all workers may be repeatedly exposed without adverse effect. The Conference of Governmental Industrial Hygienists (ACGIH) adopts threshold limit values.
toxic chemical	Chemical that can produce injury or illness through inhalation, dermal absorption, ingestion, or injection and that meets the following criteria: ?*Oral LD-50 in white rats greater than 50 mg/kg but less than 500 mg/kg; ?*Dermal LD-50 in white rabbits greater than 200 mg/kg but less than 1000 mg/kg; or ?*Inhalation LC-50 in white rats greater than 200 ppm but less than 2000 ppm (for gases or vapors) or greater than 2 mg/L but less than 20 mg/L (for dusts, fumes, or mists). Chemicals that have a higher LD-50 or LC-50 are considered to be nontoxic for the purposes of monitoring.
unstable (reactive)	Chemical that decomposes, condenses, or becomes self-reactive under conditions of shock, pressure, or temperature.
water reactive	Chemical that reacts with water to release a gas that is flammable, explosive, or a health hazard.

Chemical Management System (CMS) Inventories in HazCom Operations

Point of Contact: Chemical Management System

BNL requires that hazardous chemicals are accounted for in the <u>Chemical Management System (CMS)</u>. For additional guidance, see <u>What Chemicals Need to Be Inventoried in the CMS</u>.

1. Chemicals containers arriving on-site by the standard acquisition method are inventoried and bar coded, when applicable, at Receiving, Building 100 by the CMS Team. If manufacturer-labeled chemical containers are brought on-site by any other method, notify the CMS Team to have chemical containers inventoried and bar coded for inclusion in the CMS.

CMS Bar Code Label



2. The CMS Contact Person is responsible for chemical inventory and must ensure that chemicals in the area are used, stored, and inventoried properly. The CMS Contact Person is also responsible for ensuring that inventory is accurately recorded and up-to-date by periodically accessing the Chemical Management System (CMS) to reconcile and update inventory.

The CMS Team will periodically generate reports when there has been no change or activity in the CMS Contact Person's inventory over prolonged periods.

3. CONTAINER DELETIONS

When bar coded chemical containers are empty or designated for disposal, remove the bar code label and affix it to the Bar Code Label Removal Sheet. If the bar code label cannot be transferred to the Bar Code Label Removal Sheet, write in the bar code number and deface the bar code label before disposing of the container. Forward the Bar Code Label Removal Sheet to the CMS Team, Building 120. Bar Code Label Removal Sheets can be obtained from the CMS Team or from the Chemical Management System.

1 CONTAINER TRANSFERALS

When transferring a bar coded chemical container to another room, owner, or storage location, fill out the information on the Chemical Transfer Sheet. The new information includes the date, bar code number, contact person, organization code, building number, and room number. Do not remove the bar code label when transferring a chemical container. Forward the Chemical Transfer Sheet with the new information to the CMS Team, Building 120. Chemical Transfer Sheets can be obtained from the CMS Team or from the Chemical Management System.

5 STATIC INVENTORY

Static Inventory is a classification reserved to track chemical quantities, but not the individual container. Chemical containers that experience a high turnover/high consumption rate or containers that are always exchanged for the same type and amount (e.g., gas cylinders, cleaning chemicals in bulk storage) may be designated as static. Under this category, chemicals are inventoried using the expected maximum amount of each substance found in the area at any given time.

A **Static Inventory Posting**, containing the bar codes, is then posted in the area. The individual chemical containers are not bar coded.

Do not remove the static inventory posting. If the amounts specified on the static inventory posting deviate significantly, exceed the maximum, or a change in process occurs, contact the CMS Team.

6. RELOCATION

Chemical holdings are recorded in the CMS database under a specific building, room, and storage location. If your work area or shop is moving its operations to a new room or building, notify the CMS Team of the new location of the chemical containers. This information can be sent to the CMS Team by completing a Chemical Transfer Sheet or by contacting the CMS Team directly. The up-to-date information supplied is vital for maintaining data integrity. Chemical Transfer Sheets can be obtained from the CMS Team or from the Chemical Management System.

7. TERMINATING CMS CONTACT PERSONS

Chemical holdings are also recorded in the CMS database under a specific organization, CMS Contact Person, and life number. The Human Resources Division notifies the CMS Team of upcoming employee terminations. The CMS Team then sends the terminating Contact Person and their ES&H Coordinator a report listing their assigned chemical inventory. The Contact Person is responsible for reconciling their chemical inventory before departing and notifying the CMS Team as to its final disposition. If you retire as an employee of BNL and return as a guest, inform the CMS Team of your new guest number so that inventory can be updated accordingly.

2 TRANSFERRING CMS CONTACT PERSONS

Before transferring to another Department/Division, notify the CMS Team as to your new organization, as well as the disposition of your chemical inventory. Notify the CMS Team when a "Request for Change in Employee Status" Form (BNL F 1081) is prepared for a person on the Contact Person List.

Personal Protective Equipment (PPE) in HazCom Operations

See the <u>Personal Protective Equipment</u> Subject Area for specific guidance on obtaining, using, maintaining, and disposing of PPE at BNL.

1 Eye Protection

- ?? Use safety glasses with side shields when handling any hazardous chemical.
- ?? Use splash-proof goggles or a full-face shield when pouring corrosive liquids such as inorganic acids and bases.
- ?? Use vapor-proof goggles or a full-face respirator when handling highly toxic chemicals with the potential for vaporization or airborne particulate (outside of hoods or glove boxes).



2. Body Protection

- ?? Wear appropriate PPE when the potential for contamination of employee-owned clothing could occur. BNL-issued and laundered clothing may be used when handling hazardous chemicals when they provide adequate protection.
- ?? Wear Lab coats for HazCom Operations when handling hazardous chemicals. Do not wear Lab coats used in hazardous chemical areas outside these areas.



3. Hand Protection

For operations where contact with the chemical does not pose a significant amount of time of contact with the chemical:

- ?? Nitrile and PVC elastomers typically offer superior permeation protection over natural rubber gloves. If contact with the chemical actually occurs, the operation must stop, and the glove removed and disposed of immediately. (Note: Nitrile and PVC are free of latex sensitization hazards. Nontalc natural rubber is less hazardous).
- ?? Natural rubber gloves (surgeon or medical exam gloves) may be used for operations when handling chemicals with low toxicity (where contact with the chemical does not pose a significant risk).

For operations where there is the potential for significant contact with hazardous chemicals:

?? Select appropriate gloves based on acceptable permeation rate, breakthrough time, degradation, and dexterity. Typical operations in this class include immersion of gloves into liquids, pouring large quantities of liquids, handling large quantities of corrosive or highly toxic powders, or handling concentrated inorganic acids and bases. These gloves may be reused if properly decontaminated before storage.



4. Foot Protection

- ?? Wear safety-toed shoes when handling chemical drums or large packages of chemicals in a manner that could result in foot injury.
- ?? Sandals and open-toed shoes are prohibited during HazCom Operations at all times.
- ?? When handling cryogenic liquids, refer to <u>ES&H Standard 4.10.2</u>, <u>Flammable Liquids: Storage, Use, and Disposal</u> and <u>ES&H Standard 5.1.0</u>, <u>Nonflammable Cryogenic Liquids</u> for information on hand and eye protection.



5. In the event of a chemical exposure to the skin:

- ?? Immediately remove contaminated garment.
- ?? For small areas of skin contamination: Remove contaminated clothing. Wash the skin thoroughly with water.
- ?? For large areas of skin contamination: Remove contaminated clothing. Wash the area thoroughly in a safety shower. Call (or have someone else call) 911 for assistance.
- ?? Report all chemical exposures to the Occupational Medicine Clinic in Building 490.

Note: Consider bringing in seldom used clothes (pants, socks, and shirt) and keep them readily available in case of this type of event.

6. In the event of a chemical inhalation exposure:

Leave the area and immediately call 911 for assistance.

Chemical Storage in HazCom Operations

- 1. Flammable and combustibles (See ES&H Standard 4.10.2, Flammable Liquids: Storage, Use, and Disposal)
 - Minimize the quantities to an amount adequate for day-to-day operations.
 - Store large quantities in an NFPA-approved flammable storage cabinet.
 - Store away from oxidizers.
 - Do not store in ordinary refrigerators. A spark from the motor or light switch can ignite such a substance.
 - Use only in well-ventilated areas.
 - Remove all heat and ignition sources from the area.
 - Keep containers closed when not in use.
 - Check containers regularly for leaks.
 - Ground large containers before transferring liquids from metal containers.
- 2. Storage of any material (other than water) in aboveground or underground tanks or portable containers >/= 250 gallons are covered by the requirements found in the Storage and Transfer of Hazardous Materials Subject Area.



- **3.** Do not store hazardous chemicals over sinks where breakage could cause entry into the sanitary system.
- **4.** Segregate chemicals in storage to prevent incompatibility in flammability and reactivity in the event of accidental breakage. Refer to Examples of Incompatible Chemicals in the Hazardous Waste Management Subject Area, and sections "Explosive Materials" (page 18) and "Peroxide Forming Compounds" (page 23) in this Handbook.
- 5. Store chemicals known to be highly toxic, including those classified as carcinogens, in ventilated storage areas in unbreakable, chemically resistant secondary containers. Post the storage areas for these chemicals with a warning signs and limit access. Exposure monitoring or a hazard assessment is required.



Do not store acids and caustic liquids above eye level. A typical storage location for these types of corrosive liquids is a base cabinet under a sink or a special acid storage cabinet.



Avoid exposing chemicals to heat or sunlight. 8. Store chemicals in cabinets or shelves when not in use. Toe boards (lips) on shelves lessen the chance of accidentally dislodging bottles from the shelf. (Cabinets with metal shelves can often be converted into shelves with toe boards [lips] by turning the shelves over to place the metal structural support upwards). 9. Do not place food in chemical storage area refrigerators. These refrigerators are to be used for storage of chemicals only. Place a label on the refrigerator stating "Food Prohibited." FOR CHEMICALS ONLY NO FOOD PERMITTED Avoid excessive use of a work bench as a storage area to prevent crowding and the potential for 10. breakage of bottles during routine work on the bench. Keep storage of chemicals in exhaust hoods to a minimum. Chemicals may be stored within the 11. hood on elevated shelves or platforms (noncombustible material) that do not restrict the airflow within the hood. Do not store chemicals by mere alphabetical order without regard to the class and hazard of the 12. chemicals. Sort and store by hazard and chemical class. 13. Use **storage trays** or secondary containers to minimize the distribution of the spill should a container break or leak.

Eyewash Equipment & Emergency Showers in HazCom Operations

The use of corrosive and hazardous chemicals necessitates that emergency response capabilities are in place to ensure worker safety in the event of an accidental exposure. The following guidelines will ensure that equipment is ready and functioning in the event of an emergency. **Equipment must be suitable for the <u>quick and complete drenching or</u> flushing of the eyes and body in an emergency situation.**



BNL's goal is compliance with OSHA 29 CFR 1910.151, OSHA 29 CFR 1910.1450, and the principles in ANSI Z358.1. To meet this objective, the following <u>guidelines</u> on design and periodic testing are to be followed:

- 1. In any HazCom operation where the eyes or body could potentially be injured by <u>corrosive</u> <u>materials or formaldehyde</u>, provide equipment for quick drenching or flushing of the eyes and body (e.g., eyewash equipment and emergency showers).
- 2. Design:
 - (a.) New equipment purchases must meet the current design specifications in ANSI Z358.1. Units are to be installed within manufacturer's installation specifications.
 - (b.) Existing equipment should be upgraded to (2.a.) or replaced if its current design is not capable of drenching or flushing the eyes and body in an emergency situation.
 - (c.) Self-contained and portable eyewash stations must be serviced according to manufacturer's instructions. Limit use of self-contained and portable eyewash stations to areas where plumbed units are not feasible. An <a href="https://limit.com/li



- **3.** The optimal design for plumbed **Emergency Showers** includes the following specifications:
 - ?? 82-inch clearance from floor (208 cm);
 - ?? Spray pattern 20 inches (50.8 cm) at 60 inches (154.2 cm);
 - ?? Center of spray 16 inches (40.6 cm) from any obstruction;
 - ?? Capable of delivery of 20 gpm (75.7 lpm);
 - ?? Sufficient liquid for 15-minute flow;
 - ?? Valve designed to remain on without use of operator's hands;
 - ?? Valve shall remain on until intentionally shut off;
 - ?? Valve operates from "off" to "on" in 1 second or less;
 - ?? Actuator not more than 69 inches (173.3 cm) above the level of the user's feet:
 - ?? Accessible location no more than 10 seconds;
 - ?? Located on the same floor level as the hazard;
 - ?? Shower free of obstructions that inhibit immediate use of equipment;
 - ?? Freeze protected;
 - ?? Identified by high visibility sign;
 - ?? Flushing fluid delivery tepid.



4. The optimal design for plumbed **Eyewash Equipment** includes the following:

- ?? Controlled flow to both eyes simultaneously;
- ?? Flow not injurious to eyes;
- ?? Nozzles are protected from airborne hazards and mechanism does not require a separate motion to remove:
- ?? Enough room provided to allow eyelids to be held open with hands:
- ?? Nozzles between 33 inches (83.3 cm) and 45 inches (114.3 cm) from floor;
- ?? Nozzles a minimum of 6 inches (15.3 cm) from nearest wall or obstruction;
- ?? Capable of delivery of 0.4 gpm (1.5 lpm);
- ?? Sufficient liquid for 15-minute flow;
- ?? Valve designed to remain on without use of operator's hands;
- ?? Valve shall remain on until intentionally shut off;
- ?? Valve operates from "off" to "on" in 1 second or less;
- ?? Accessible location no more than 10 seconds;
- ?? Located on the same level as the hazard, with path free of obstructions that may inhibit immediate use of equipment;
- ?? Shower free of obstructions that inhibit immediate use of equipment;
- ?? Freeze protected;
- ?? Identified by high visibility sign;
- ?? Flushing fluid delivery tepid.

5 Periodic Testing

- (a.) In HazCom Operations areas with <u>corrosive chemicals</u> or <u>formaldehyde</u>, <u>activate</u> eyewash equipment <u>weekly</u>.
 Have plumbed eyewash equipment and emergency showers <u>inspected annually</u> to ensure ANSI Z-358.1 conformance.
- (b.) In HazCom Operations areas with non-corrosive hazardous chemicals, <u>activate</u> eyewash equipment at least every <u>3</u> months.

Have plumbed eyewash equipment and emergency showers inspected annually to ensure ANSI Z-358.1 conformance.

Post the <u>Eye Wash Activation/Inspection Sign</u> (or use an equivalent method) to ensure the periodic activation and inspection testing of equipment.

Verify that the *BNL Inspection Office Inspection Tag* for eyewash equipment and emergency showers indicates the equipment has been inspected.





Example of an Eye Wash Activation/Inspection Sign or Label

Eye Wash used for Corrosive Chemicals or Formaldehyde:

EYE WASHActivation/Inspection

Activate this eye wash weekly to verify operation.

Have this equipment tested annually for compliance with SBMS *Working With Chemicals* Subject Area guidance.

Eye Wash used for HazCom Areas with non-corrosive chemicals:

EYE WASHActivation/Inspection

Activate this eye wash quarterly to verify operation.

Have this eyewash tested annually for compliance with SBMS *Working With Chemicals* Subject Area guidance.

Explosive Materials

Acetylides of heavy metals Picramide Dvnamite EDNP (ethyl 4,4-dinitropentanoate) Aluminum ophorite explosive Picratol Ammonium nitrate explosive mixtures Erythritol tetranitrate explosives Picric acid Esters of nitro-substituted alcohols Picryl chloride Aromatic nitro-compound explosive EGDN (ethlyene glycol dinitrate) Picryl fluoride Potassium nitroaminotetrazole Ammonium perchlorate having particle Ethyl tetryl Silver acetylide size less than 15 microns Fulminates of mercury, gold, silver, platinum Ammonium picrate Guanyl nitrosamino guanyl tetrazene Silver azide ANFO (ammonium nitrate-fuel oil) Guanyl nitrosamine guanylidene hydrazine Silver oxalate Heavy metal azides Silver styphnate BAEF (1,2-bis (2,2-difluoro-2-Hexanitrodiphenylamine Silver tartrate nitroacetoxyethane) Black pow der Hexanitrostilbene Silver tetrazene Blasting agents, nitro-carbo-nitrates Hvdrazoic acid Sodium amatol KDNBF (potassium dinitrobenzo-furoxane) BTNEC (bis (trinitroethyl) carbonate) Sodium dinitro-ortho-cresolate BTNEN (bis (trinitroethyl) nitramine) Lead azide Sodium picramate BTNN (1,2,4 butanetriol trinitrate) I ead mannite Styphnic acid Butyl tetryl Lead mononitroresorcinate TATB (triaminotrinitrobenzene) TEGDN (triethlene glycol dinitrate) Calcium nitrate explosive mixture Lead picrate Copper acetylide Lead styphnate Tetrazene Cyanuric triazide Magnesium ophorite Tetranitrocarbazole Cyclotrimethylenetrinitramine Mannitol hexanitrate Tetryl (2,4,6 tetranitro-N-metylaniline) Cyclotetramethlenetetranitramine TMETN (trimetylolethane trinitrate) MDNP (metyl 4,4-dinitropentanoate) Cyclotol Mercury oxalate TNEF (Trinitroethyl formal) Diaminotrinitrobenzene Mercury tartrate TNEOC (trinitroethylorthocarbonate) Diazodinitrophenol NIBTN (nitroisobutametriol trinitrate) TNEOF (trinitroethyl orthoformate) Diethyleneglycol dinitrate TNT (trinitrotoluene) Nitrogen trichloride Dinitroethyleneurea Nitrogen tri-iodide Trinitroanisole Dinitroglycerine Nitroglycerin Trinitrobenzene Dinitrophenol Nitroglycide Trinitrobenzoic acid Dinitrophenolates Nitroglycol Trinitrocresol Dinitrophenyl hydrazine Nitrostarch Trinitro-meta-cresol Dinitroresorcinol Nitrourea Trinitronaphthalene Dipicryl sulfone Organic nitramines Trinitrophenetol Dipicryl amine Organic peroxides Trinitrophloroglucinol DNDP (dinitropentano nitrile) Picramic acid and its salts Trinitro resorcinol DNPA (2,2-dinitropropyl acrylate) Urea nitrate Release of harmful pressure on shock or exposure to ignition source. Main Hazard First Aid Immediately call 911. Begin immediate and continuous flushing with water until Fire Rescue transports to a hospital. Remove potentially contaminated clothing during the flushing. For minor skin contact during working hours (e.g., limited exposure to fingers): Begin immediate and continuous flushing with water and call OMC at x-3670. Follow their instructions. Remove potentially contaminated clothing during the flushing. For inhalation: Immediately call 911. Move to fresh air. Fire Rescue will transport to a hospital. **Special Provisions** ?? No working alone. ?? Identify the location of explosives on the Fire Rescue Run Card system and Green Hazard Information Placard at doorways.

Working With Chemicals, Handbook on Chemical Use in HazCom Operations

Work Planning and Control Documentation (Work Permit or ESR)	Work Planning and Control Documentation (Work Permit or ESR) must specifically address how PPE, Spill Response, First Aid, and the Special Provisions of this section are met.
Spill Response Prerequisites	Evacuate area. Call 911. Do not attempt clean-up of concentrated acid.
Personal Protective Equipment Prerequisites	Face shield required.

Hydrofluoric Acid

Main Hazard	Hydrofluoric Acid (HF) causes severe skin burns (often painless). Two percent solutions can cause burns. HF deeply penetrates before disassociating. Burns may involve underlying bone. Systemic fluoride ion poisoning from severe burns is associated with low calcium, high potassium, and low magnesium in the blood, and sudden death. Inhalation can cause fluid in the lungs and severe respiratory burns.
First Aid	Immediately call 911. Begin immediate and continuous flushing with water until Fire Rescue can transport to a hospital. Remove potentially contaminated clothing during the flushing.
	For minor skin contact during working hours (e.g., limited exposure to fingers): Begin immediate & continuous flushing with water and call OMC at x-3670. Follow their instructions. Remove potentially contaminated clothing during the flushing.
	For inhalation: Immediately call 911. Move to fresh air. Wait for Fire Rescue to provide transporation to a hospital.
Special Provisions	 ?? Where HF is used, an eye wash station and shower must be within the immediate area. ?? HF Burn Kits (or worksite calcium gluconate gel) are not recommended. The OMC-approved method of treatment is immediate and continual flushing with water followed by medical attention. ?? No working alone. ?? Identify the location of Hydrofluoric acid on the <u>Fire Rescue Run Card system</u> and Green Hazard Information Placard at doorways.
Work Planning and Control Documentation (Work Permit or ESR)	Work Planning and Control Documentation (Work Permit or ESR) must specifically address how PPE, Spill Response, First Aid, and the Special provisions of this section are met.
Storage	Store with mineral acids (except Sulfuric Acid). Do not store with organic material. Do not transfer concentrated acid to glass or metal containers.
Spill Response Prerequisites	Evacuate area. Call 911. Do not attempt clean-up of concentrated acid.
Personal Protective Equipment Prerequisites	Gloves: Splash: Nitrile disposable glove; Immersion: PVC, Neoprene are required. Lab coat or long-sleeved shirt is required. Face shield and body covering suit required when pouring concentrated acid.

Metallic Azides

Hazard	Hazard: explosive Uses: Plating with metals like lead
Special Provisions	 Labeling of hoods Wash-down systems Decontamination Plan must be addressed in Work Planning and Control documentation.
Work Planning and Control Documentation (Work Permit or ESR)	Work Planning and Control Documentation (Work Permit or ESR) must specifically address how all special provisions of this section are met.
Engineering Controls Prerequisites	Unless process knowledge of the entire history is known, contact the IH Representative for testing. Ventilation equipment that is contaminated by testing will be labeled with the date and "Azide contaminated."
Equipment Monitoring Prerequisites	Use of Azide acid (above 100 mg per year), must be done in specifically designed hood with a "wash down system," unless there is permission within the Work Planning review process with concurrence of Working with Chemicals SME .
	Testing of surface contamination is required: o At demolition or modification of any hood or local exhaust duct, o On an annual basis while Azide are in use (above 100 mg per year), o At the end of a project or that used Azides.

Perchlorates/Perchloric Acid

Use of perchloric acid can create deposits of highly explosive metal perchlorates in hoods, ducts, fan housing, and other system components. Hammering, banging, and parts disassembly can result in a very hazardous explosion and subsequent injury of maintenance or construction personnel. To prevent this hazard, requirements and limitations on perchloric acid use in exhaust systems are necessary. In particular, when perchloric acid is used in quantities that can create the explosion hazard in the exhaust system, all work must be done in specifically designed perchloric acid/ perchlorate hoods with wash-down systems.

Special Provisions	 Surface wipe sampling Labeling of hoods Wash-down systems Decontamination Plan must be addressed in Work Planning and Control documentation.
Work Planning and Control Documentation (Work Permit or ESR)	Work Planning and Control Documentation (Work Permit or ESR) must specifically address how all <i>Special Provisions</i> of this section are met.
Engineering Controls Prerequisites	A. Quantitative Surface Wipe Analysis is required for all lab hoods and exhaust ventilation equipment, unless process knowledge of the entire history of the equipment can verify that perchlorates/perchloric acids were never used in the system. Equipment that by process knowledge is known to be non- contaminated does not need to be tested.
	B. Unless process knowledge of the entire history is known, contact the IH Representative for testing. Ventilation equipment found to be contaminated by testing is labeled with the date and "Perchlorate contaminated." Develop a plan for future action with the IH Representative.
	Ventilation equipment that is tested and found to be non-contaminated will be labeled with date and "Perchlorate hazard free".
Equipment Monitoring Prerequisites	Use of perchloric acid (above 10 ml per year) must be done in specifically designed hood with a wash-down system, unless there is permission within the Work Planning review process with concurrence of Working with Chemicals SME .
	Testing of surface contamination is required: o Before demolition or modification of any hood or local exhaust duct, o On an annual basis while perchloric acid are in use (above 10 ml per year), o At the end of a project or work that used perchloric acid.

Peroxide Forming Compounds

General Hazard

- ?? Peroxides form in solvents, reagents, gases, and solids by the autoxidation or peroxidation of a peroxidizable compound with molecular oxygen. This hazard can be insidious and has caused many accidents.
- ?? Peroxides in solution at concentrations up to about one percent do not normally present thermal or shock hazards. Such solutions may be safely disposed of or treated to remove peroxides. However, should crystals form in a peroxidizable liquid or discoloration occur in a peroxidizable solid, peroxidation may have occurred and the product should be considered extremely dangerous and destroyed without opening the container. Contact your Departmental ES&H Coordinator for assistance in arranging for disposal through the Waste Management Division.

Materials Likely to Form Peroxides in Storage- List A

LIST A: Severe Peroxide Hazard on Storage with Exposure to Air

List A presents the most hazardous peroxidizable solvents. These compounds may explode even without being concentrated. (Affix date label upon receipt and test for peroxide within three months of receipt. Contact ES&H Coordinator if tested positive. Re-date material if tested negative.

- ?? Diisopropyl ether (isopropyl ether)
- ?? Divinyl acetylene (DVA)
- ?? Divinyl ether
- ?? Vinylidene chloride (1,1-dichloroethylene)'

Materials Likely to Form Peroxides in Storage- List B

LIST B: Peroxide Hazard on Concentration. Observe Proper Precautions Before Distilling or Evaporating.

List B contains solvents which form peroxides that require concentration (such as through distillation or evaporation) in order to present a hazard.

(Affix date label upon receipt and test for peroxide within 12 months of opening. Contact ES&H Coordinator if tested positive at a level greater than or equal to 100 ppm. Re-date material if tested negative or below 100 ppm.)

- ?? Acetal (diethyl acetal)
- ?? Cumene (isopropyl benzene)
- ?? Cyclohexene
- ?? Cyclooctene
- ?? Cyclopentene
- ?? Decalin (decahydronaphthalene)
- ?? Diacetylenes (butadiyne, etc.)
 Dicyclopentadiene
- ?? Diethyl ether (ether)
- ?? Diethylene glycol dimethylether (diglyme)
- ?? Dioxane (p-dioxane, 1,4-dioxane)

- ?? Ethylene glycol dimethyl ether (glyme) Ethyleneglycol ether acetates
- ?? Ethylene glycol monoethers (cellosolves)
- ?? Furan
- ?? Methyl acetylene
- ?? Methylcylopentane
- ?? Methyl isobutyl ketone
- ?? Tetrahydrofuran (THF)
- ?? Tetralin (tetrahydronaphthalene)
- ?? Vinyl ethers

Materials Likely to Form Peroxides in Storage- LIST C

LIST C: Hazard of Rapid Polymerization Initiated by Internally Formed Peroxides 1, 2

List C is made up of vinyl monomers which may form internal peroxides that can then initiate rapid polymerization of the bulk monomers. (Affix date label upon receipt and test for peroxide within 12 months of opening.) Contact ES&H Coordinator if tested positive at a level greater than or equal to 100 ppm. Re-date material if tested negative or below 100 ppm.

- ?? Acrylic acid
- ?? Acrylonitrile
- ?? Chloroprene (2-chloro-1,3-butadiene)
- ?? Methyl methacrylate
- ?? Styrene
- ?? Vinyl acetate
- ?? Vinylpyridine
- ?? Vinylidene chloride

Materials Likely to Form Peroxides in Storage -Peroxidizable Gases

Peroxidizable Gases

The following gases pose a potential hazard of rapid polymerization initiated by internally formed peroxides:

- ?? Butadiene
- ?? Chlorotrifluoroethylene
- ?? Methylacetylene (propyne)
- ?? Tetrafluoroethylene (TFE)
- ?? Vinylacetylene
- ?? (MVA) Vinylchloride

Although air will not enter a gas cylinder in which gases are stored under pressure, these gases are sometimes transferred from the original cylinder to another; it is difficult to be sure that there is no residual air in the receiving container. Put an inhibitor into any such secondary cylinder before one of these gases is transferred into it; the supplier can suggest inhibitors to be used. The hazard posed by these gases is much greater if there is a liquid phase in such a secondary container, and even inhibited gases that have been put into a secondary container under conditions that create a liquid phase should be discarded within 12 months.

Materials Likely to Form Peroxides in Storage- Reactive, Oxidizable Solids

Reactive, Oxidizable Solids

- ?? Potassium (K),
- ?? Potassium Amide (KNH₂),
- ?? Sodium (Na),
- ?? Sodium Amide (NaNH₂)

Store and handle these highly reactive materials only under a hydrocarbon solvent (e.g., hexane, xylene, mineral oil). Avoid all contact with water or humid air, since the hydrogen gas released upon reaction with water can cause a fire. Reaction of sodium with oxygen forms sodium peroxide (Na $_2$ O $_2$), and reaction of potassium with oxygen forms superoxide (KO $_2$), but these cannot be tested by the conventional peroxide tests.

Special Provisions

Labeling

All compounds in Lists A, B, and C must bear the dates when the containers were

¹ Store Polymerizable monomers with a polymerization inhibitor from which the monomers can be separated by distillation just before use.

Although common acrylic monomers, such as acrylonitrile, acrylic acid, ethyl acrylate, and methyl acrylate can form peroxides, they have not been reported to develop hazardous levels in normal use and storage.

first received and opened. The individual researcher affixes the appropriate information on the label upon receipt or delivery of the chemical. **Special Provisions Inventory Control** Each supervisor ensures all List A compounds are tested or properly disposed within three months of opening or receipt (whichever occurs first) and all List B and C compounds are tested or properly disposed within 12 months of opening. All compounds addressed by this section must continue to be tested on the same schedule (every three or 12months) once they are initially tested. If any List A compound tests positive for peroxide at any level, or if any List B or C compound tests positive for peroxide at or above a level of 100 ppm (0.01%), the Department ES&H Coordinator must be contacted for guidance. All materials testing below these levels must be re-dated with this information on their label. **Special Provisions Distillation and Evaporation Precautions** ?? Test all List A or B compounds for peroxide before distillation or evaporation (or treated to positively ensure peroxide destruction). If the material tests positive, it must be disposed of or treated to remove the peroxides. Add a suitable polymerization inhibitor before distilling any List C material. ?? Most accidents associated with distillation of peroxidizable compounds have occurred when peroxides have become concentrated in the distillation residue. It is therefore essential to never distill a peroxidizable solvent to a dry residue. One solution for compounds showing no more than a trace of peroxide on testing is to discontinue the distillation when a 10 per cent heel remains. Another solution is to add a high molecular weight inerting solvent which will not distill, such as mineral oil or a phthatate ester. This solvent will act as a desensitizing diluent for residual peroxides when distillation is ?? In addition to safety glasses, a shield when evaporating or distilling mixtures that may contain peroxides. **Special Provisions Detection of Peroxides** The following tests can detect most (but not all) peroxy compounds, including all hydroperoxides (Reference: "Prudent Practices in the ," National Research Council, National Academy Press, Washington, DC, 1995): a) Add 1 to 3 milliliters (ml) of the liquid to be tested to an equal volume of acetic acid, add a few drops of 5% aqueous potassium iodide solution, and shake. The appearance of a yellow-to-brown color indicates the presence of peroxides. Alternatively, addition of 1 ml of a freshly prepared 10% solution of potassium iodide to 10 ml of an organic liquid in a 25-mL glass cylinder should produce a yellow color if peroxides are present. b) Add 0.5 ml of the liquid to be tested to a mixture of 1 ml of 10% aqueous potassium iodide solution and 0.5 ml of dilute hydrochloric acid to which has been added a few drops of starch solution just before the test. The appearance of a blue or blue-black color within a minute indicates the presence of peroxides. c) Peroxide test strips, which turn to an indicative color in the presence of peroxides, are available commercially. Note that these strips must be airdried until the solvent evaporates and then exposed to moisture for proper operation. None of these tests should be applied to materials (such as metallic potassium)

	that may be contaminated with ingraphic paravides
	that may be contaminated with inorganic peroxides.
Work Planning and Control Documentation (Work Permit or ESR)	Work Planning and Control Documentation (Work Permit or ESR) must specifically address how all special provisions of this section are met.
Labeling	Containers are labeled with most recent of "Received Date," "Opened Date," or "Tested Date" (or equivalent record log).
Waste Disposal Prerequisites	Prior to submitting a <u>Waste Control Form</u> , the container is tested within the last 12 months. Notify WMD on the <u>Waste Control Form</u> of containers that cannot be tested.
Removal of Peroxides	The following guidance is from "Prudent Practices in the Laboratory," National Research Council, National Academy Press, Washington, D.C., 1995.
	a) Overview and Caution (CAUTION: Peroxides are particularly dangerous. Only knowledgeable workers should carry out these procedures.) Peroxides can be removed from a solvent by passing it through a column of basic activated alumina, by treating it with indicating Molecular Sieves, or by reduction with ferrous sulfate. Although these procedures remove hydroperoxides, which are the principle hazardous contaminants of peroxide-forming solvents, they do not remove dialkyl peroxides, which may also be present in low concentrations. Commonly used peroxide reagents, such as acetyl peroxide, benzoyl peroxide, t-butyl hydroperoxide, and di-t-butyl peroxide, are less dangerous than the adventitious peroxides formed in solvents.
	b) Removal of Peroxides with Alumina A 2 x 33 cm column filled with 80 g of 80-mesh basic activated alumina is usually sufficient to remove all peroxides from 100 to 400 ml of solvent, whether watersoluble or water-insoluble. After passage through the column, test the solvent for peroxide content. Peroxides formed by air oxidation are usually decomposed by the alumina, not merely absorbed on it. However, for safety, it is best to slurry the wet alumina with a dilute acidic solution of ferrous sulfate before it is property discarded.
	c) Removal of Peroxides with Molecular Sieves
	Reflux 100 ml of the solvent with 5 g of 4- to 8-mesh indicating activated 4A Molecular Sieves for several hours under nitrogen. The sieves are separated from the solvent and require no further treatment because the peroxides are destroyed during their interaction with the sieves.
	d) Removal of Peroxides with Ferrous Sulfate A solution of 6 g of FeSO ₄ -7H ₂ O, 6 ml of concentrated sulfuric acid, and 11 ml of water is stirred with 1 L of water-insoluble solvent until the solvent no longer gives a positive test for peroxides. Usually only a few minutes are required. Dialkyl peroxides can be destroyed by this reagent as well as by aqueous sodium hydrogen sulfate, sodium hydroxide, or ammonia. However, diacyl peroxides with low solubility in water, such as dibenzoyl peroxide, react very slowly. A better reagent is a solution of sodium iodide or potassium iodide in glacial acetic acid.

e) Destruction of Diacyl Peroxides

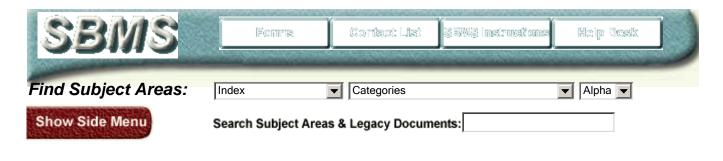
For 0.01 mol of diacyl peroxide, 0.022 mol (I 0% excess) of sodium or potassium iodide is dissolved in 70 ml of glacial acetic acid, and the peroxide added gradually with stirring at room temperature. The solution is rapidly darkened by the formation of iodine. After a minimum of 30 minutes, the solution may be properly discarded.

Most dialkyl peroxides (ROOR) do not react readily at room temperature with ferrous sulfate, iodide, ammonia, or the other reagents mentioned above. However, these peroxides can be destroyed by a modification of the iodide procedure.

f) Destruction of Dialkyl Peroxides

One milliliter of 36% (w/v) hydrochloric acid is added to the above acetic acid/potassium iodide solution as an accelerator, followed by 0.01 mol of the dialkyl peroxide. The solution is heated to 90 to 100°C on a steam bath over the course of 30 minutes and held at that temperature for 5 hours, before being properly discarded.

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Subject Area: Chemicals, Working With

Handbook on Chemical Use in Laboratories (Lab Standard)

Effective Date: May 2004

Point of Contact: Industrial Hygiene, ES&H Coordinator

The Handbook on Chemical Use in Laboratories (Lab Standard) is available as a PDF file.

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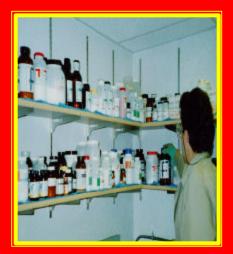
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BROOKHAVEN

Brookhaven National Laboratory

Handbook on

Chemical Use in



Laboratories

(OSHA Laboratory Standard)

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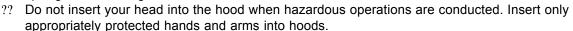
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General Rules for Laboratory Scale Use of Chemicals

1. Conduct operations with hazardous chemicals in a functioning laboratory hood, glove box, or other engineering control setting. Do not conduct operations with hazardous chemicals on lab benches. Examples of operations with hazardous chemicals are reactions, pouring, evaporation, or other vapor, mist, fume, or dust-generating operations.



- 2. Limit work with hazardous chemicals on laboratory benches to operations such as opening packing boxes, preparing labels for containers, handling closed containers of chemicals, and preparing nonhazardous test media or equipment (i.e., operations that do not have the potential to result in employee exposure to hazardous levels of chemicals).
- **3.** Keep laboratory hoods free of excessive equipment and chemical storage containers.
 - ?? Handle chemicals at least 6 inches into the hood.
 - ?? Keep equipment, boxes, and bottles at least 6 inches from the front face of the hood. Do not obstruct the flow of air into the slot in the rear of the hood.
 - ?? Chemicals may be stored within the hood on elevated shelves or platforms (noncombustible material) that do not restrict the airflow within the
 - hood. Do not store chemicals in hoods with sinks, unless provisions are made to prevent spillage from flowing into the sink.



- ?? Lower the sash to protect the eyes from a direct path to hazardous operations where splashes or impact could occur. Do not open "sash hoods" beyond the point indicated on the "face velocity test" sticker when conducting hazardous operations.
- ?? Have your lab hood tested for "face velocity" annually.
- **4.** Provide engineering controls or additional ventilation for oven, autoclaves, gas chromatographs, mass spectrometers, and other equipment, if the process conducted within the apparatus causes hazardous levels of contaminants to be produced within the occupied laboratory space.
- 5. Do not bring or consume food and beverages in laboratory chemical-handling areas. Do not store food in chemical laboratory refrigerators. Do not store chemicals in break room and kitchen refrigerators.
- **6.** Do not store bottles of corrosive chemicals (e.g., acids and bases) above eye level.
- **7.** Do not mouth pipette chemicals. Use auto-pipeting devices or pipetters.



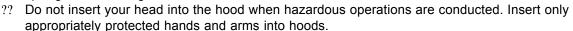
8. Use appropriate PPE to prevent eye and skin contact, ingestion, and inhalation. See the SBMS Personal Protective Equipment Subject Area.

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8. Use appropriate PPE to prevent eye and skin contact, ingestion, and inhalation. See the SBMS Personal Protective Equipment Subject Area.

7. Use a tray to surround a bottle or vessel to contain the hazardous liquids in the event of a spill or leak. This tray is referred to as secondary containment. It is not necessary to label the secondary containment unless its construction covers the label on the primary vessel.

Note: Placing more than one container into the same tray is acceptable only if the chemicals are compatible.



8. Carcinogens must be labeled with warning that the chemical is a potential carcinogen. Examples of appropriate labels/signs are:





(9/2004)

Chemical Container Labeling in Laboratories

Do not remove or deface labels on containers (bottles, boxes, bags, drums) received from manufacturers and distributors unless they are replaced with a label that contains equivalent wording on the contents.

Manufacturer's Label



Note: Re-using a container once it has been cleaned is acceptable. In that case, it is acceptable and required to deface the original label.

Label stationary containers (e.g., tanks or vessels) in a laboratory with a label that identifies the name of the chemical within the vessel. Adding the hazards of the chemical (e.g., toxicity, fire hazard, reactivity, stability) is advisable.



When processes require the transfer of all or a portion of a chemical to a new container, <u>identify the chemical name</u> on the new container. Adding the hazard of the chemical (e.g., toxicity, fire hazard, reactivity, stability) is advisable.



- 4. Alternative Means of Labeling: Using codes or numbers on bottles or vessels as a means of labeling is permitted. There must be a logbook, laboratory record, sample sheet, or other written record of the codes or numbers that allows all users to know the contents of the container. All workers in the lab need to be familiar with the numbering technique so they can identify the contents.
 - For example: If a bottle is labeled "6-JQP-123," its code name must link to the sixth lab book, the notebook must be numbered "6-JQP," and page 123 of that notebook must list information on the chemical.
- **Temporary Use Containers:** When a container (e.g., bucket, bottle, or beaker) is filled for temporary use, it does not have to be labeled if all of the following apply:
 - ?? It will be used only by the person who has filled the temporary container;
 - ?? There is no possibility for misidentification with other containers;
 - ?? It will be not used beyond one shift;
 - ?? It will not be left unattended in an area where other persons are located. Examples of temporary use containers are chromatograph sample bottles, test tubes, daily use of graduated cylinders, beakers, volumetric flasks, and culture plates.



6. Guidance for Small Sample Vials and Ampoules: Individual labels on small containers may be impractical. Labeling a sample holder that holds numerous small containers of similar chemicals with a group label is permitted.

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	 (100°F) and below 60°C (140°F). ?? Class IIIA liquids include those having flash points at or above 60°C (140°F) and below 93°C (200°F). ?? Class IIIB liquids include those having flash points at or above 93°C (200°F).
compressed gas	Any mixture of gases in a container with an absolute pressure exceeding 40 psi at 70°F or 104 psi at 130°F, or a liquid having a vapor pressure exceeding 40 psi at 100°F.
corrosive	A material that causes destruction or alteration of human tissue at the site of contact.
cryogenic liquid	A refrigerated liquefied gas having a boiling point colder than -90°C (-130°F) at 101.3pKa (14.7 psi) absolute.
explosives	Chemicals that cause a sudden, almost instantaneous release of pressure, gas, and heat when subjected to sudden shock, pressure, or high temperature.
flammable gas	A gas that is flammable in a mixture of 13% or less (by volume) with air; or the flammable range with air is wider than 2 percent regardless of the lower limit.
flammable liquid	A liquid having a flash point below 100°F (37.8°C) and having a vapor pressure not exceeding 40 lb. per sq. in. (absolute) (2068 mm Hg) at 100°F (37.8°C). Class I liquids are subdivided as follows:
	 ?? Class IA includes those having flash points below 73°F (22.8°C) and having a boiling point below 100°F (37.8°C). ?? Class IB includes those having flash points below 73°F (22.8°C) and having a boiling point below 100°F (37.8°C). ?? Class IC includes those having flash points below 73°F (22.8°C) and below 100°F (37.8°C).
flammable solid	A substance that is:
	?? Thermally unstable and can undergo a strongly exothermic decomposition even without participation of oxygen;?? Readily combustible and can cause a fire through friction, such as
	matches; ?? Any material with a burning rate faster than 2.2 mm (0.087 in) per second; ?? Any metal powder that can be ignited and react over the whole length of a sample in 10 minutes or less.
irritant	matches; ?? Any material with a burning rate faster than 2.2 mm (0.087 in) per second; ?? Any metal powder that can be ignited and react over the whole length of a
irritant organic peroxide	matches; ?? Any material with a burning rate faster than 2.2 mm (0.087 in) per second; ?? Any metal powder that can be ignited and react over the whole length of a sample in 10 minutes or less.
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organic peroxide oxidizer permissible exposure limits	matches; ?? Any material with a burning rate faster than 2.2 mm (0.087 in) per second; ?? Any metal powder that can be ignited and react over the whole length of a sample in 10 minutes or less. Chemical that has a reversible inflammatory effect on living tissue. Compounds that release oxygen readily and are capable of violent or explosive decomposition when exposed to air. A material that initiates or promotes combustion in other materials, thereby causing fire either of itself or through the release of oxygen or other gases. Airborne concentrations of substances that represent conditions under which it is believed nearly all workers may be repeatedly exposed, daily, without adverse effects. PELs represent time-weighted average concentrations, usually expressed in units of mg/m³ or parts per million (ppm) for an 8-hour workday within a 40-hour
organic peroxide oxidizer permissible exposure limits (PELs)	matches; ?? Any material with a burning rate faster than 2.2 mm (0.087 in) per second; ?? Any metal powder that can be ignited and react over the whole length of a sample in 10 minutes or less. Chemical that has a reversible inflammatory effect on living tissue. Compounds that release oxygen readily and are capable of violent or explosive decomposition when exposed to air. A material that initiates or promotes combustion in other materials, thereby causing fire either of itself or through the release of oxygen or other gases. Airborne concentrations of substances that represent conditions under which it is believed nearly all workers may be repeatedly exposed, daily, without adverse effects. PELs represent time-weighted average concentrations, usually expressed in units of mg/m³ or parts per million (ppm) for an 8-hour workday within a 40-hour work week. Any chemical that is combustible, explosive, flammable, pyrophoric, unstable

	developing fetus.	
short-term exposure limit® (STEL®)	Amount of a chemical to be safely exposed to over a 15-minute period.	
target organ toxin	Chemical that adversely affects a particular organ in the body.	
threshold limit value® (TLV®)	A time-weighted average airborne concentration for a normal 8-hour work day and 40-hour work week to which nearly all workers may be repeatedly exposed without adverse effect. The Conference of Governmental Industrial Hygienists (ACGIH) adopts threshold limit values.	
toxic chemical	Chemical that can produce injury or illness to an individual through inhalation, dermal absorption, ingestion, or injection and that meets the following criteria: ?? Oral LD-50 in white rats greater than 50 mg/kg but less than 500 mg/kg; ?? Dermal LD-50 in white rabbits greater than 200 mg/kg but less than 1000 mg/kg; ?? Inhalation LC-50 in white rats greater than 200 ppm but less than 2000 ppm (for gases or vapors) or greater than 2 mg/L but less than 20 mg/L (for dusts, fumes, or mists). Chemicals that have a higher LD-50 or LC-50 are considered to be nontoxic for the purposes of monitoring.	
unstable (reactive)	Chemical that decomposes, condenses, or becomes self-reactive under conditions of shock, pressure, or temperature.	
water reactive	Chemical that reacts with water to release a gas that is flammable, explosive, or a health hazard.	

Chemical Management System (CMS) Inventories in Laboratories

Point of Contact: Chemical Management System

BNL requires that all chemicals are accounted for in the <u>Chemical Management System (CMS)</u>. For additional guidance, see What Chemicals Need to Be Inventoried in the CMS.

1. Chemical containers arriving on-site by the standard acquisition method are inventoried and bar coded when applicable at Receiving, Building 100, by the CMS Team. If manufacturer-labeled chemical containers are brought on-site by any other method, notify the CMS Team to have chemical containers inventoried and bar coded for inclusion in the CMS.

CMS Bar Code Label



2. CMS Contact Persons are responsible for their chemical inventory and must ensure that chemicals in their area are used, stored, and inventoried properly. CMS Contact Persons also are responsible for ensuring that their inventory is accurately recorded and up-to-date by periodically accessing the Chemical Management System (CMS) to reconcile and update inventory. The CMS Team will generate reports when there has been no change or activity in the CMS Contact Person's inventory over prolonged periods.

3. CONTAINER DELETIONS

When bar coded chemical containers are empty or designated for disposal, remove the bar code label and affix it to the Bar Code Label Removal Sheet. If the bar code label cannot be transferred to the Bar Code Label Removal Sheet, write in the bar code number and deface the bar code label before disposing of the container. Forward the Bar Code Label Removal Sheet to the CMS Team, Building 120. Bar Code Label Removal Sheets can be obtained from the CMS Team or from the Chemical Management System.

4 CONTAINER TRANSFERALS

When transferring a bar coded chemical container to another room, researcher, or storage location, fill out the information on the Chemical Transfer Sheet. The new information includes the date, bar code number, contact person, organization code, building number, and room number. Do not remove the bar code label when transferring a chemical container. Forward the Chemical Transfer Sheet with the new information to the CMS Team, Building 120. Chemical Transfer Sheets can be obtained from the CMS Team or from the Chemical Management System.

5. STATIC INVENTORY

Static Inventory is a classification reserved to track chemical quantities, but not the individual container. Chemical containers that experience a high turnover/high consumption rate or containers that are always exchanged for the same type and amount (e.g., gas cylinders, cleaning chemicals in bulk storage) may be designated as static. Under this category, chemicals are inventoried using the expected maximum amount of each substance found in the area at any given time.

A **Static Inventory Posting**, containing the bar codes, is then posted in the area. The individual chemical containers are not bar coded.

Do not remove the static inventory posting. If the amounts specified on the static inventory posting deviate significantly, exceed the maximum, or a change in process occurs, contact the CMS Team.

6. LABORATORY RELOCATION

Chemical holdings are recorded in the CMS database under a specific building, room, and storage location. If your laboratory or shop is moving its operations to a new room or building, notify the CMS Team of the new location of the chemical containers. This information can be sent to the CMS Team by completing a Chemical Transfer Sheet or by contacting the CMS Team directly. The up-to-date information supplied is vital for maintaining data integrity. Chemical Transfer Sheets can be obtained from the CMS Team or from the Chemical Management System.

7. TERMINATING CMS CONTACT PERSONS

Chemical holdings are also recorded in the CMS database under a specific organization, CMS Contact Person, and life number. The Human Resources Division notifies the CMS Team of upcoming employee terminations. The CMS Team then sends the terminating Contact Person and their ES&H Coordinator a report listing their assigned chemical inventory. The Contact Person is responsible for reconciling their chemical inventory before departing and notifying the CMS Team as to its final disposition. If you retire as an employee of the Laboratory and return as a guest, inform the CMS Team of your new guest number so that inventory can be updated accordingly.

8. TRANSFERRING CMS CONTACT PERSONS

Before transferring to another Department/Division, notify the CMS Team as to your new organization, as well as the disposition of your chemical inventory. Notify the CMS Team when a "Request for Change in Employee Status" Form (BNL F 1081) is prepared for a person on the Contact Person List.

Personal Protective Equipment (PPE) in Laboratories

See the <u>Personal Protective Equipment</u> Subject Area for specific guidance on obtaining, using, maintaining, and disposing of PPE at BNL. Limit work with chemicals without PPE to operations that do not have the potential to result in employee exposure to hazardous levels of chemicals.

1 Eye Protection

- ?? Use safety glasses with side shields when handling any hazardous chemical.
- ?? Use splash-proof goggles or a full-face shield when pouring corrosive liquids (e.g., inorganic acids and bases).
- ?? Use vapor-proof goggles or a full-face respirator when handling highly toxic chemicals with the potential for vaporization or airborne particulate (outside of laboratory hoods or glove boxes).



2 Body Protection

- ?? Wear appropriate PPE when the potential for contamination of employee-owned clothing could occur. Laboratory-issued and laundered clothing may be used when handling hazardous chemicals when they provide adequate protection.
- 2? Wear Lab coats in laboratories when handling hazardous chemicals. Do not wear Lab coats used in hazardous chemical areas outside these areas.



3 Hand Protection

For operations where contact with the chemical does not pose a significant amount of time of contact with the chemical:

- ?? Nitrile and PVC elastomers typically offer superior permeation protection over natural rubber gloves. If contact with the chemical actually occurs, immediately stop the operation, and remove and dispose the glove. (Note: Nitrile and PVC are free of latex sensitization hazards. Non-talc natural rubber is less hazardous.)
- ?? Natural rubber gloves (e.g., surgeon or medical exam gloves) may be used for operations when handling chemicals with low toxicity (where contact with the chemical does not pose a significant risk).

For operations where there is the potential for significant contact with hazardous chemicals:

?? Select appropriate gloves based on acceptable permeation rate, breakthrough time, degradation, and dexterity. Typical operations in this class include immersion of gloves into liquids, pouring large quantities of liquids, handling large quantities of corrosive or highly toxic powders, or handling concentrated inorganic acids and bases. These gloves may be reused if properly decontaminated before storage.



△ Foot Protection

- ?? Wear safety-toed shoes when the handling of chemical drums or large packages of chemicals could cause foot injury.
- ?? Sandals and open-toe shoes are prohibited in laboratories at all times.
- ?? When handling cryogenic liquids, refer to <u>ES&H Standard 4.10.2</u>, <u>Flammable Liquids: Storage, Use, and Disposal</u> and <u>ES&H Standard 5.1.0</u>, <u>Nonflammable Cryogenic Liquids</u> for information on hand and eye protection.



5. In the Event of Chemical Exposure to the Skin:

- ?? Immediately remove contaminated garment.
- ?? For small areas of skin contamination: Remove contaminated clothing. Wash the skin thoroughly with water.
- ?? For large areas of skin contamination: Remove contaminated clothing. Wash the area thoroughly in a safety shower. Call (or have someone else call) 911 for assistance.
- ?? Report all chemical exposures to the Occupational Medicine Clinic in Building 490.

Note: Consider bringing in some seldom-used clothes (pants, socks, and shirt) and keep them handy in case of this type of event.

6. In the Event of a Chemical Inhalation Exposure:
Leave the area and immediately call 911 for assistance.

Chemical Storage in Laboratories

- 1. Flammable and combustibles (See <u>ES&H Standard 4.10.2</u>, Flammable Liquids: Storage, <u>Use</u>, and <u>Disposal</u>):
 - Minimize quantities to an amount that is adequate for day-to-day operations.
 - Store large quantities in an NFPA-approved flammable storage cabinet.
 - Store away from oxidizers.
 - Do not store in ordinary refrigerators. A spark from the motor or light switch can ignite such a substance.
 - Use only in well-ventilated area.
 - Remove all heat and ignition sources from the area.
 - Keep containers closed when not in use.
 - Check containers regularly for leaks.
 - Ground large containers before transferring liquids from metal containers.
- 2. Storage of any material (other than water) in aboveground or underground tanks or portable containers >/= 250 gallons is covered by the requirements found in the Storage and Transfer of Hazardous Materials Subject Area.



- 3. Do not store hazardous chemicals over sinks where breakage could cause entry into the sanitary system.
- 4. Segregate chemicals in storage to prevent incompatibility in flammability and reactivity in the event of accidental breakage. Refer to Examples of Incompatible Chemicals in the Hazardous Waste Management Subject Area, and sections "Explosive Materials" and "Peroxide-Forming Compounds" in this Handbook.
- 5. Store chemicals known to be highly toxic, including those classified as carcinogens, in ventilated storage areas and in unbreakable, chemically resistant secondary containers. Post the storage areas for these chemicals with warning and limited access signs.



Do not store acids and caustic liquids above eye level. A typical storage location for these types of corrosive liquids is a base cabinet under a sink or a special acid storage cabinet.



7. Avoid exposing chemicals to heat or sunlight.

Store chemicals in cabinets or shelves when not in use. Toe boards (0.5 inch high lips on the front of the shelf) on shelves lessen the chance of accidentally dislodging bottles from the shelf. (Cabinets with metal shelves can often be converted into shelves with toe boards [lips] by turning the shelves over to place the metal structural support upwards).



9. Do not place food in laboratory refrigerators. Laboratory refrigerators are to be used for storage of chemicals only. Place a label on the refrigerator stating "No Food Permitted."



- Avoid excessive use of lab bench as a storage area to prevent crowding and the potential for breakage of bottles during routine work on the bench.
- Keep storage of chemicals in laboratory hoods to a minimum. Chemicals may be stored within the hood on elevated shelves or platforms (noncombustible material) that do not restrict the airflow within the hood.
- 12. Do not store chemicals by mere alphabetical order without regard to the class and hazard of the chemicals. Sort and store by hazard and chemical class.
- 13. Use **storage trays** or secondary containers to minimize the distribution of the spill should a container break or leak.

In the event of a major spill, evacuate the area and from a safe location and call 911 for the BNL Emergency Services Division response team. For more guidance, see the Emergency Preparedness and Spill Response Subject Areas.



Eyewash Equipment & Emergency Showers in Laboratories

The use of corrosive and hazardous chemicals necessitates that emergency response capabilities are in place to ensure worker safety in the event of an accidental exposure. The following guidelines ensure that equipment is ready and functioning in the event of an emergency. This includes equipment for the <u>quick and complete drenching or flushing of the</u> eyes and body in an emergency situation.

BNL's goal is compliance with OSHA 29 CFR 1910.151, OSHA 29 CFR 1910.1450, and the principles in ANSI Z358.1. To meet this objective, the following <u>guidelines</u> on design and periodic testing are to be followed:



- 1. In any laboratory where <u>corrosive materials or formaldehyde</u> could potentially injure the eyes or body, provide equipment for quick drenching or flushing of the eyes and body (e.g., eyewash equipment and emergency showers).
- 2. Design:
 - (a.) New equipment purchases must meet the current design specifications in ANSI Z358.1. Units are to be installed within manufacturer's installation specifications.
 - (b.) Existing equipment should be upgraded to (2.a.) or replaced if its current design is not capable of drenching or flushing the eyes and body in an emergency situation.
 - (c.) Self-contained and portable eyewash stations must be serviced according to manufacturer's instructions. Limit use of self-contained and portable eyewash stations to areas where plumbed units are not feasible. The <a href="https://limit.com/l



- **3.** The optimal design for plumbed **Emergency Showers** includes the following:
 - ?? 82-inch clearance from floor (208 cm);
 - ?? Spray pattern 20 inches (50.8 cm) at 60 inches (154.2 cm);
 - ?? Center of spray 16 inches (40.6 cm) from any obstruction:
 - ?? Capable of delivery of 20 gpm (75.7 lpm);
 - ?? Sufficient liquid for 15-minute flow;
 - ?? Valve designed to remain on without use of operator's hands;
 - ?? Valve remains on until intentionally shut off;
 - ?? Valve operates from "off" to "on" in 1 second or less;
 - ?? Actuator not more than 69 inches (173.3 cm) above the level of the user's feet;
 - ?? Accessible location no more than 10 seconds;
 - ?? Located on the same floor level as the hazard:
 - ?? Shower free of obstructions that inhibit immediate use of equipment;
 - ?? Freeze-protected;
 - ?? Identified by high visibility sign;
 - ?? Flushing fluid delivery tepid.



The optimal design for plumbed **Eyewash Equipment** includes the following:

- ?? Controlled flow to both eyes simultaneously;
- ?? Flow not injurious to eyes;
- ?? Nozzles protected from airborne hazards; mechanisms do not require a separate motion to remove;
- ?? Enough room provided to allow eyelids to be held open with hands:
- ?? Nozzles between 33 inches (83.3 cm) and 45 inches (114.3 cm) from floor;
- ?? Nozzles a minimum of 6 inches (15.3 cm) from nearest wall or obstruction;
- ?? Capable of delivery of 0.4 gpm (1.5 lpm);
- ?? Sufficient liquid for 15-minute flow;
- ?? Valve designed to remain on without use of operator's hands;
- ?? Valve shall remain on until intentionally shut off;
- ?? Valve operates from "off" to "on" in 1 second or less;
- ?? Accessible location no more than 10 seconds away;
- ?? Located on the same level as the hazard, path free of obstructions that inhibit immediate use of equipment;
- ?? Shower free of obstructions that inhibit immediate use of equipment;
- ?? Freeze-protected;
- ?? Identified by high visibility sign;
- ?? Flushing fluid delivery tepid.

5. Periodic Testing

- (a.) In laboratories with <u>corrosive chemicals</u> or <u>formaldehyde</u>, <u>activate</u> eyewash equipment <u>weekly</u>. Have plumbed eyewash equipment and emergency showers inspected annually to assure ANSI Z-358.1 conformance.
- (b.) In laboratories with hazardous chemicals, <u>activate</u> eyewash equipment at least every <u>3 months</u>.
 Have plumbed eyewash equipment and emergency showers <u>inspected annually</u> to assure ANSI Z-358.1 conformance.

Post the <u>Eye Wash Activation/Inspection Sign</u> (or use an equivalent method) to ensure the periodic activation and inspection testing of equipment.

Verify that the *BNL Inspection Office Inspection Tag* for eyewash equipment and emergency showers indicates that the equipment has been inspected.





Example of an Eye Wash Activation/Inspection Sign or Label

Eye Wash used for Corrosive Chemicals or Formaldehyde:

EYE WASHActivation/Inspection

Activate this eye wash weekly to verify operation.

Have this equipment tested annually for compliance with SBMS *Working With Chemicals* Subject Area guidance.

Eye Wash used for HazCom Areas with non-corrosive chemicals:

EYE WASHActivation/Inspection

Activate this eye wash quarterly to verify operation.

Have this eyewash tested annually for compliance with SBMS *Working With Chemicals* Subject Area guidance.

Specific Chemical Hazards Explosive Materials

Acetylides of heavy metals Aluminum ophorite explosive Ammonium nitrate explosive mixtures Aromatic nitro-compound explosive mixtures Ammonium perchlorate having particle size less than 15 microns Ammonium picrate ANFO (ammonium nitrate-fuel oil) BAEF (1,2-bis (2,2-difluoro-2- nitroacetoxyethane) Black powder	Dynamite EDNP (ethyl 4,4-dinitropentanoate) Erythritol tetranitrate explosives Esters of nitro-substituted alcohols EGDN (ethlyene glycol dinitrate) Ethyl tetryl Fulminates of mercury, gold, silver, platinum Guanyl nitrosamino guanyl tetrazene Guanyl nitrosamine guanylidene hydrazine Heavy metal azides Hexanitrodiphenylamine Hexanitrostilibene	Picramide Picratol Picric acid Picryl chloride Picryl fluoride Potassium nitroaminotetrazole Silver acetylide Silver azide Silver oxalate Silver styphnate Silver tartrate Silver tetrazene
Blasting agents, nitro-carbo-nitrates BTNEC (bis (trinitroethyl) carbonate) BTNEN (bis (trinitroethyl) nitramine) BTNN (1,2,4 butanetriol trinitrate) Butyl tetryl Calcium nitrate explosive mixture Copper acetylide Cyanuric triazide Cyclotrimethylenetrinitramine Cyclotetramethlenetetranitramine Cyclotol Diaminotrinitrobenzene	Hydrazoic acid KDNBF (potassium dinitrobenzo-furoxane) Lead azide Lead mannite Lead mononitroresorcinate Lead picrate Lead styphnate Magnesium ophorite Mannitol hexanitrate MDNP (metyl 4,4-dinitropentanoate) Mercury oxalate Mercury tartrate	Sodium amatol Sodium dinitro-ortho-cresolate Sodium picramate Styphnic acid TATB (triaminotrinitrobenzene) TEGDN (triethlene glycol dinitrate) Tetrazene Tetranitrocarbazole Tetryl (2,4,6 tetranitro-N-metylaniline) TMETN (trimetylolethane trinitrate) TNEF (Trinitroethyl formal) TNEOC (trinitroethylorthocarbonate)
Diazodinitrophenol Diazodinitrophenol Diethyleneglycol dinitrate Dinitroethyleneurea Dinitrophenol Dinitrophenol Dinitrophenolates Dinitrophenyl hydrazine Dinitroresorcinol Dipicryl sulfone Dipicryl amine DNDP (dinitropentano nitrile) DNPA (2,2-dinitropropyl acrylate)	NIBTN (nitroisobutametriol trinitrate) Nitrogen trichloride Nitrogen tri-iodide Nitroglycerin Nitroglycide Nitroglycide Nitroglycol Nitrostarch Nitrourea Organic nitramines Organic peroxides Picramic acid and its salts	TNEOC (trinitroethyl orthoformate) TNEOF (trinitroethyl orthoformate) TNT (trinitrotoluene) Trinitroanisole Trinitrobenzene Trinitrobenzoic acid Trinitrocresol Trinitro-meta-cresol Trinitronaphthalene Trinitrophenetol Trinitrophloroglucinol Trinitro resorcinol Urea nitrate
Main Hazard	Release of harmful pressure on shock or exposure to ignition source.	
First Aid	Immediately call 911. Begin immediate and continuous flushing with water until Fire Rescue transports to a hospital. Remove potentially contaminated clothing during the flushing. For minor skin contact during working hours (e.g., limited exposure to fingers): Begin immediate and continuous flushing with water and call OMC at x-3670. Follow their instructions. Remove potentially contaminated clothing during the flushing. For inhalation, immediately call 911. Move to fresh air. Fire Rescue transports to a hospital.	
Special Provisions		
	?? Identify the location of explosives on the <u>Fire Rescue Run Card</u> <u>System</u> and Green Hazard Information Placard at doorways.	
Work Planning and Control Documentation (Work Permit or ESR)	Work Planning and Control Documentation (Work Permit or ESR) must specifically address how PPE, Spill Response, First Aid, and the special provisions of this section are met.	

Working With Chemicals, Handbook on Chemical Use in Laboratories

Spill Response Prerequisites	Evacuate area. Call 911. Do not attempt clean-up of concentrated acid.
Personal Protective Equipment Prerequisites	Faceshield required.

Specific Chemical Hazards Hydrofluoric Acid

Main Hazard	Hydrofluoric Acid (HF) causes severe skin burns (often painless). Two percent solutions can cause burns. HF deeply penetrates before disassociating. Burns may involve underlying bone. Systemic fluoride ion poisoning from severe burns is associated with low calcium, high potassium, and low magnesium in blood, and sudden death. Inhalation can cause fluid in the lungs and severe respiratory burns.
First Aid	Immediately call 911. Begin immediate and continuous flushing with water until Fire Rescue transports to a hospital. Remove potentially contaminated clothing during the flushing.
	For minor skin contact during working hours (e.g., limited exposure to fingers): Begin immediate and continuous flushing with water and call OMC at x-3670. Follow their instructions. Remove potentially contaminated clothing during the flushing.
	For inhalation: Immediately call 911. Move to fresh air. Fire Rescue transports to a hospital.
Special Provisions	 ?? Where HF is used, an eye wash station and shower must be within the immediate area. ?? HF Burn Kits (or worksite calcium gluconate gel) are not recommended. The OMC-approved method of treatment is immediate and continual flushing with water followed by medical attention. ?? No working alone. ?? Identify the location of HF on the <u>Fire Rescue Run Card System</u> and Green Hazard Information Placard at doorways.
Work Planning and Control Documentation (Work Permit or ESR)	Work Planning and Control Documentation (Work Permit or ESR) must specifically address how PPE, Spill Response, First Aid, and the Special provisions of this section are met.
Storage	Store with mineral acids (except Sulfuric Acid). Do not store with organic material. Do not transfer concentrated acid to glass or metal containers.
Spill Response Prerequisites	Evacuate area. Call 911. Do not attempt clean-up of concentrated acid.
Personal Protective Equipment Prerequisites	Gloves: Splash: Nitrile disposable glove; Immersion: PVC, Neoprene are required. Lab coat or long-sleeved shirt is required. Faceshield required when pouring concentrated acid.

Specific Chemical Hazards

Metallic Azides

Hazard	Hazard: explosive Uses: Plating with metals like lead.	
Special Provisions	 Labeling of hoods; Wash down systems; Decontamination Plan must be addressed in Work Planning and Control documentation. 	
Work Planning and Control Documentation (Work Permit or ESR)	Work Planning and Control Documentation (Work Permit or ESR) must specifically address how all special provisions of this section are met.	
Engineering Controls Prerequisites	Unless process knowledge of the entire history is known, contact the IH Representative for testing. Ventilation equipment that is contaminated by testing will be labeled with the date and "Azide Contaminated."	
Equipment Monitoring Prerequisites	Use of Azide acid (above 100 mg per year) must be done in a specifically designed hood with a "wash down system," unless there is permission within the Work Planning review process with concurrence of Working With Chemicals SME.	
	Testing of surface contamination is required: o At demolition or modification of any hood or local exhaust duct, o On an annual basis while Azides are in use (above 100 mg per year), o At the end of a project that used Azides.	

Specific Chemical Hazards

Perchlorates/Perchloric Acid

Use of perchloric æid can create deposits of highly explosive metal perchlorates in hoods, ducts, fan housing, and other system components. Hammering, banging, and parts disassembly can result in very hazardous explosion and subsequent injury of maintenance or construction personnel. To prevent this hazard, requirements and limitations on perchloric acid use in exhaust systems are made. In particular, when perchloric acid is used in quantities that can create the explosion hazard in the exhaust system, all work must be done in specifically designed "perchloric acid/ perchlorate" hoods with wash down systems.

Work Planning and Control Documentation (Work Permit or ESR)	 Surface wipe sampling; Labeling of hoods; Wash down systems; Decontamination Plan must be addressed in Work Planning and Control documentation. Work Planning and Control Documentation (Work Permit or ESR) must specifically address how all Special Provisions of this section are met. 	
Engineering Controls Prerequisites	 A. Quantitative Surface Wipe analysis is required for all lab hoods and exhaust ventilation equipment, unless process knowledge of the entire history of the equipment can verify that perchlorates/perchloric acid were never used in the system. Equipment that by process knowledge is known to be noncontaminated does not need to be tested. B. Unless process knowledge of the entire history is known, contact the IH Representative for testing. Ventilation equipment found to be contaminated by testing is labeled with the date and "Perchlorate Contaminated." Develop a plan for future action with the IH Representative. Copy to IH SOP. 	
Equipment Monitoring Prerequisites	Use of perchloric acid (above 10 ml per year) must be done in specifically designed hood with a "wash down system" unless there is permission within the Work Planning review process with concurrence of Working With Chemicals SME. Testing of surface contamination is required: O Before demolition or modification of any hood or local exhaust duct, On an annual basis while perchloric acid are in use (above 10 ml per	
	year), o At the end of a project or work that used perchloric acid.	

Specific Chemical Hazards

Peroxide-Forming Compounds

General Hazard Peroxides form in solvents, reagents, gases, and solids by the autoxidation or peroxidation of a peroxidizable compound with molecular oxygen. This hazard can be insidious and has caused many accidents. Peroxides in solution at concentrations up to about one percent do not normally present thermal or shock hazards. Such solutions may be safely disposed of or treated to remove peroxides. However, should crystals form in a peroxidizable liquid or discoloration occur in a peroxidizable solid, peroxidation may have occurred and the product should be considered extremely dangerous and should be destroyed without opening the container. Contact your Department ES&H Coordinator for assistance in arranging for disposal through the Waste Management Division. LIST A: Severe Peroxide Hazard on Storage With Exposure to Air **Materials Likely to** List A presents the most hazardous peroxidizable solvents. These compounds Form Peroxides in Storage-List A may explode even without being concentrated. Affix date label upon receipt and test for peroxide within three months of receipt. Contact ES&H Coordinator if tested positive. Re-date material if tested negative. Diisopropyl ether (isopropyl ether) Divinyl acetylene (DVA) ?? Divinvl ether ?? Vinylidene chloride (1,1-dichloroethylene) **Materials Likely to** LIST B: Peroxide Hazard on Concentration. Observe Proper Precautions Form Peroxides in Before Distilling or Evaporating. Storage-List B List B contains solvents that form peroxides that require concentration (such as through distillation or evaporation) in order to present a hazard. Affix date label upon receipt and test for peroxide within 12 months of opening. Contact ES&H Coordinator if tested positive at a level greater than or equal to 100 ppm. Re-date material if tested negative or below 100 ppm. ?? Acetal (diethyl acetal) ?? Ethylene glycol dimethyl ether ?? Cumene (isopropyl benzene) (glyme) Ethyleneglycol ether ?? Cyclohexene acetates ?? Ethylene glycol monoethers ?? Cyclooctene (cellosolves) ?? Cyclopentene ?? Furan ?? Decalin (decahydronaphthalene) ?? Methyl acetylene ?? Diacetylenes (butadiyne, etc.) ?? Methylcylopentane Dicyclopentadiene ?? Methyl isobutyl ketone ?? Diethyl ether (ether) ?? Tetrahydrofuran (THF) ?? Diethylene glycol dimethylether ?? Tetralin (tetrahydronaphthalene) (diglyme) ?? Vinyl ethers ?? Dioxane (p-dioxane, 1,4-dioxane)

Materials Likely to Form Peroxides in Storage- LIST C

LIST C: Hazard of Rapid Polymerization Initiated by Internally Formed Peroxides ^{1, 2}

List C is made up of vinyl monomers which may form internal peroxides that can then initiate rapid polymerization of the bulk monomers. (Affix date label upon receipt and test for peroxide within 12 months of opening.) Contact ES&H Coordinator if tested positive at a level greater than or equal to 100 ppm. Re-date material if tested negative or below 100 ppm.

- ?? Acrylic acid
- ?? Acrylonitrile
- ?? Chloroprene (2-chloro-1,3-butadiene)
- ?? Methyl methacrylate
- ?? Styrene
- ?? Vinyl acetate
- ?? Vinylpyridine
- ?? Vinylidene chloride

Materials Likely to Form Peroxides in Storage -Peroxidizable Gases

Peroxidizable Gases

The following gases pose a potential hazard of rapid polymerization initiated by internally formed peroxides:

- ?? Butadiene
- ?? Chlorotrifluoroethylene
- ?? Methylacetylene (propyne)
- ?? Tetrafluoroethylene (TFE)
- ?? Vinvlacetylene
- ?? (MVA) Vinylchloride

Although air will not enter a gas cylinder in which gases are stored under pressure, these gases are sometimes transferred from the original cylinder to another in the laboratory, and it is difficult to be sure that there is no residual air in the receiving container. Put an inhibitor into any such secondary cylinder before one of these gases is transferred into it; the supplier can suggest inhibitors to be used. The hazard posed by these gases is much greater if there is a liquid phase in such a secondary container, and even inhibited gases that have been put into a secondary container under conditions that create a liquid phase should be discarded within 12 months.

Materials Likely to Form Peroxides in Storage- Reactive, Oxidizable Solids

Reactive, Oxidizable Solids

- ?? Potassium (K)
- ?? Potassium Amide (KNH₂)
- ?? Sodium (Na)
- ?? Sodium Amide (NaNH₂)

Store and handle these highly reactive materials only under a hydrocarbon solvent (e.g., hexane, xylene, mineral oil). Avoid all contact with water or humid air, since the hydrogen gas released upon reaction with water can cause a fire. Reaction of sodium with oxygen forms sodium peroxide (Na $_2$ O $_2$), and reaction of potassium with oxygen forms superoxide (KO $_2$), but these can not be tested by the conventional peroxide tests.

Special Provisions

Labeling

¹ Store Polymerizable monomers with a polymerization inhibitor from which the monomers can be separated by distillation just before use.

Although common acrylic monomers, such as acrylonitrile, acrylic acid, ethyl acrylate, and methyl acrylate can form peroxides, they have not been reported to develop hazardous levels in normal use and storage.

All compounds in Lists A, B, and C must bear the dates when the containers were first received and opened. The individual laboratory researcher affixes the appropriate information on the label upon receipt or delivery of the chemical. **Special Provisions Inventory Control** Each supervisor responsible for a laboratory ensures all List A compounds are tested or properly disposed within three months of opening or receipt (whichever occurs first), and all List B and C compounds are tested or properly disposed within 12 months of opening. All compounds addressed by this section must continue to be tested on the same schedule (every three or 12 months) once they are initially tested. If any List A compound tests positive for peroxide at any level, or if any List B or C compound tests positive for peroxide at or above a level of 100 ppm (0.01%), the Department ES&H Coordinator must be contacted for guidance. All materials testing below these levels must be re-dated with this information on their label. **Special Provisions Distillation and Evaporation Precautions** ?? Test all List A or B compounds for peroxide before distillation or evaporation (or treated to positively ensure peroxide destruction). If the material tests positive, it must be disposed of or treated to remove the peroxides. Add a suitable polymerization inhibitor before distilling any List C material. Most accidents associated with distillation of peroxidizable compounds have occurred when peroxides have become concentrated in the distillation residue. It is therefore essential to never distill a peroxidizable solvent to a dry residue. One solution for compounds showing no more than a trace of peroxide on testing is to discontinue the distillation when a 10% heel remains. Another solution is to add a high molecular, weight-inerting solvent that will not distill, such as mineral oil or a phthatate ester. This solvent will act as a desensitizing diluent for residual peroxides when distillation is complete. In addition to safety glasses, use a shield when evaporating or distilling mixtures that may contain peroxides. **Special Provisions Detection of Peroxides** The following tests can detect most (but not all) peroxy compounds, including all hydroperoxides (Reference: "Prudent Practices in the Laboratory." National Research Council, National Academy Press, Washington, D.C., 1995): a) Add 1 to 3 milliliters (ml) of the liquid to be tested to an equal volume of acetic acid, add a few drops of 5% aqueous potassium iodide solution, and shake. The appearance of a yellow-to-brown color indicates the presence of peroxides. Alternatively, addition of 1 ml of a freshly prepared 10% solution of potassium iodide to 10 ml of an organic liquid in a 25-mL glass cylinder should produce a yellow color if peroxides are present. b) Add 0.5 ml of the liquid to be tested to a mixture of 1 ml of 10% aqueous potassium iodide solution and 0.5 ml of dilute hydrochloric acid to which a few drops of starch solution have been added just before the test. The appearance of a blue or blue-black color within a minute indicates the presence of peroxides. c) Peroxide test strips, which turn to an indicative color in the presence of peroxides, are available commercially. Note that these strips must be air-dried until the solvent evaporates and then exposed to moisture for proper operation. None of these tests should be applied to materials (such as metallic potassium)

	that may be contaminated with inorganic peroxides.	
Work Planning and Control Documentation (Work Permit or ESR)	Work Planning and Control Documentation (Work Permit or ESR) must specifically address how all special provisions of this section are met.	
Labeling	Containers are labeled with most recent of "Received Date," "Opened Date," or "Tested Date" (or equivalent record log).	
Waste Disposal Prerequisites	Prior to submitting a Nonradioactive Waste Control Form, the container is tested within the last 12 months. Notify WMD on the Nonradioactive Waste Control Form of containers that cannot be tested.	
Removal of Peroxides	The following guidance is from "Prudent Practices in the Laboratory," National Research Council, National Academy Press, Washington, D.C., 1995.	
	a) Overview and Caution (CAUTION: Peroxides are particularly dangerous. Only knowledgeable laboratory workers should carry out these procedures.) Peroxides can be removed from a solvent by passing it through a column of basic activated alumina, by treating it with indicating Molecular Sieves, or by reduction with ferrous sulfate. Although these procedures remove hydroperoxides, which are the principle hazardous contaminants of peroxide-forming solvents, they do not remove dialkyl peroxides, which may also be present in low concentrations. Commonly used peroxide reagents, such as acetyl peroxide, benzoyl peroxide, t-butyl hydroperoxide, and di-t-butyl peroxide, are less dangerous than the adventitious peroxides formed in solvents.	
	b) Removal of Peroxides with Alumina A 2x33 cm column filled with 80 g of 80-mesh basic activated alumina is usually sufficient to remove all peroxides from 100 to 400 ml of solvent, whether water-soluble or water-insoluble. After passage through the column, test the solvent for peroxide content. Peroxides formed by air oxidation are usually decomposed by the alumina, not merely absorbed on it. However, for safety, it is best to slurry the wet alumina with a dilute acidic solution of ferrous sulfate before it is properly discarded. c) Removal of Peroxides with Molecular Sieves	
	Reflux 100 ml of the solvent with 5 g of 4- to 8-mesh indicating activated 4A Molecular Sieves for several hours under nitrogen. The sieves are separated from the solvent and require no further treatment because the peroxides are destroyed during their interaction with the sieves.	

d) Removal of Peroxides with Ferrous Sulfate

A solution of 6 g of FeSO₄-7H₂O, 6 ml of concentrated sulfuric acid, and 11 ml of water is stirred with 1 L of water-insoluble solvent until the solvent no longer gives a positive test for peroxides. Usually only a few minutes are required.

Dialkyl peroxides can be destroyed by this reagent as well as by aqueous sodium hydrogen sulfate, sodium hydroxide, or ammonia. However, diacyl peroxides with low solubility in water, such as dibenzoyl peroxide, react very slowly. A better reagent is a solution of sodium iodide or potassium iodide in glacial acetic acid.

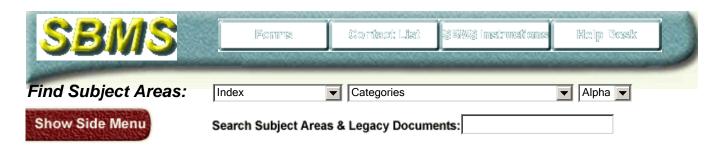
e) Destruction of Diacyl Peroxides

For 0.01 mol of diacyl peroxide, 0.022 mol (I 0% excess) of sodium or potassium iodide is dissolved in 70 ml of glacial acetic acid, and the peroxide added gradually with stirring at room temperature. The solution is rapidly darkened by the formation of iodine. After a minimum of 30 minutes, the solution may be properly discarded.

Most dialkyl peroxides (ROOR) do not react readily at room temperature with ferrous sulfate, iodide, ammonia, or the other reagents mentioned above. However, these peroxides can be destroyed by a modification of the iodide procedure.

f) Destruction of Dialkyl Peroxides

One milliliter of 36% (w/v) hydrochloric acid is added to the above acetic acid/potassium iodide solution as an accelerator, followed by 0.01 mol of the dialkyl peroxide. The solution is heated to 90 to 100°C on a steam bath over the course of 30 minutes and held at that temperature for 5 hours, before being properly discarded.



Subject Area: Chemicals, Working With

Highly Acute Toxin Sign

Effective Date: April 2002

Point of Contact: Safety & Health Services Division Manager

The Highly Acute Toxin Sign is provided as a PDF file.

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Highly Acute Toxin Designated Area

Authorized Personnel Only

2.0/1718e011.pdf (04/2002)



Subject Area: Chemicals, Working With

Reproductive Toxin Sign

Effective Date: December 2002

Point of Contact: Safety & Health Services Division Manager

The Reproductive Toxin Sign is provided as a PDF file.

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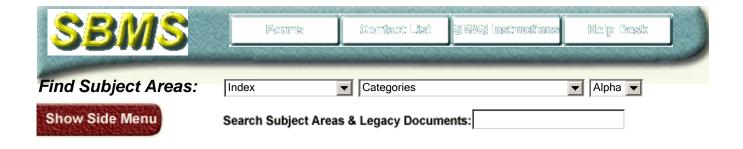


Reproductive Toxin

Designated Area

Authorized Personnel Only

(04/2002)



Definitions: Chemicals, Working With

Effective Date: May 2004

Point of Contact: Industrial Hygiene Manager

Term	Definition	
administrative controls	Methods of minimizing inhalation and physical contact exposures through measures such as: Periods away from contaminant or physical stressor through job rotation, limitation of exposure time, or work/rest regimens; Laboratory safety and health procedures; Signs and postings.	
chemical	Any element, chemical compound, or mixture of elements and/or compounds.	
Chemical Hygiene Officer	An employee who is designated by BNL to provide technical guidance in the development and implementation of the Chemical Hygiene Plan and the Hazard Communication Program. BNL Chemical Hygiene Officer is the Chemical Safety Subject Matter Expert (SME).	
Chemical Hygiene Plan	A written program developed and implemented by BNL to set forth procedure, equipment, and work practices that protect employees from the health and safety hazards presented by hazardous chemicals in laboratory settings.	
Chemical Management System (CMS)	BNL's chemical management system that enables retrieval of MSDS, chemical forms, location of chemicals and chemical contact persons, communication with the CMS team, and other information on chemicals and chemical resources.	
CMS chemical owner	Person who is documented in the CMS system as being responsible for the chemical.	
engineering controls	Methods of controlling exposures by eliminating or reducing the presence of the chemical. It includes measures such as: • Substituting a less hazardous chemical;	

	 Isolating or enclosing a process or work operation (e.g., use of a closed system, glove box, or toxic gas cabinet); Using wet methods to reduce aerosol generation; Using local exhaust ventilation at the point of generation or laboratory fume hood.
exposure	Contact with a chemical, biological, radiological, or physical hazard. Exposures may be acute (large doses over a short period) or chronic (small doses over a long period).
Hazard Communication Program	A written document that describes BNL's implementation of the OSHA Hazard Communication Standard. The Plan consists of Section Using the Hazard Communication Plan for Working With Chemicals in HazCom Operations of this Subject Area and the exhibit Handbook on Chemical Use in HazCom Operations.
hazardous chemical	Any chemical that poses a physical or health hazard when: • Statistically significant evidence based on at least one study conducted in accordance with established scientific principles shows that acute or chronic health effects may occur in exposed employees; • Scientifically valid evidence shows that the chemical is: • a combustible liquid; • a compressed gas; • explosive; • flammable; • an organic peroxide; • an oxidizer; • pyrophoric; • unstable (reactive); • water-reactive.
hazcom area	Any area where an employee may be exposed to chemicals under normal conditions of use or in a foreseeable emergency, except in areas where there is laboratory use of chemicals, covered under laboratory standard area.
hazcom employee	A worker who may be exposed to hazardous chemicals under normal working/operating conditions or in foreseeable emergencies. Office workers who encounter hazardous chemicals only in nonroutine, isolated instances are not hazcom employees.

	Homoutine, isolated mistarioes are not hazeom employees.
health hazard	Any substance that may cause acute or chronic health effects in exposed individuals. Such substances include the following: Carcinogens; Toxic or acutely toxic agents; Reproductive or developmental toxins; Irritants; Corrosives; Sensitizers; Liver, kidney, and nervous system toxins; Agents that act on the blood-forming systems; Agents that damage the lungs, skin, eyes, or mucous membranes; Biologically produced chemical agents.
highly toxic chemical	To be classified as "highly toxic," a chemical must meet the following criteria: • Oral LD-50 in white rats equal to or less than 50 mg/kg; • Dermal LD-50 in white rabbits equal to or less than 200 mg/kg; or • Inhalation LC-50 in white rats equal to or less than 200 ppm (for gases or vapors) or 2 mg/L (for dusts, fumes or mists).
laboratory standard operation	 Laboratory use of chemicals which meets the following conditions: Chemical manipulations are easily carried out by one person; Multiple chemical procedures or chemicals are used; The procedures involved are not part of a production process, nor in any way simulate a production process; Protective laboratory practices and equipment are available and in common use to minimize the potential for employee exposure to hazardous chemicals.
Material Safety Data Sheet (MSDS)	Written or printed materials, supplied by the manufacturer or BNL, containing information on chemical identity, physical and chemical properties, physical hazards, health hazards, protective safety methods, and emergency procedures.
Materials of Trade (MOT)	Certain hazardous materials (e.g., hazardous chemicals or other hazardous material that will be consumed by a staff member's work), when used in direct support of BNL's business, may be transferred from one location to another by a staff member for his or her own use as Materials of Trade (MOT). The regulations for transporting MOT are less restrictive and based on a quantity limit for specific Department of Transportation hazard classes. The BNL Materials of Trade (MOT) exhibit in the Transportation of Hazardous Materials Offsite Subject Area provides the quantity limits for MOT

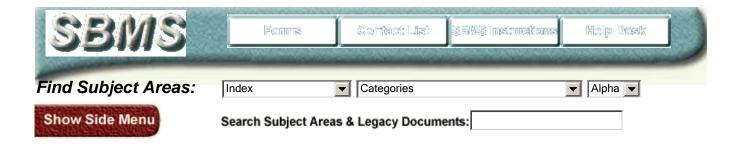
	נטוווווטווון עספט מנ טועב נוומנ כמוו עם נומווסףטונפט.	
NFPA Fire Diamond Label	A labeling system that provides information on health, fire, reactivity, and other hazards associated with the chemical.	
OSHA Regulated Chemicals	Chemicals for which OSHA has promulgated specific regulations in 29 CFR 1910 or 29 CFR 1926.	
OSHA Select Carcinogen	See carcinogen.	
Particularly Hazardous Substance	 A chemical with one or more of the following designations: Carcinogen; Reproductive toxin (see the <u>CMS Reproductive Toxins Table</u>); Substance with a high degree of acute toxicity (see the <u>CMS Highly Acute Toxin Table</u>). 	
Personal Protective Equipment (PPE)	A control measure that places a barrier between the worker and the hazards, and is used when engineering and administrative controls are not sufficient to control exposure; while engineering controls are being installed; and when engineering and administrative controls are not possible. Examples of PPE are gloves, respirators, lab coats, coveralls, and protective suits.	
secondary container	Any container into which chemicals are transferred.	
Secondary containment	Trays or outer jacketing surrounding a container used to minimize or contain a spill if the container breaks or leaks.	

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Revision History: Chemicals, Working With

Point of Contact: Safety & Health Services Division Manager

Revision History of This Subject Area

Date	Description	Management System
September 2004 Minor Rev. 4.1	The Eyewash Activation/Inspection Sign was replaced in the Handbook on Chemical Use in Laboratories (Lab Standard).	Worker Safety and Health
May 2004	This revision replaces Interim Procedure, "Eyewash Fountains and Emergency Showers" and Environment, Safety and Health (ESH) Standard 2.2.1, Laboratory Workplace Standard for Nonradioactive Toxic Substances. All sections of this subject area are replaced with the following new sections: • Determining the Applicability of the Hazard Communication Program or the Chemical Hygiene Plan for Laboratories • Using the Chemical Hygiene Plan in Laboratories (Lab Standard), and • Using the Hazard Communication Plan for Working With Chemicals in HazCom Operations	Worker Safety and Health
	The following handbooks are new:	

	 Handbook on Chemical Use in HazCom Operations and Handbook on Chemical Use in Laboratories Key changes and additions include: Eye Washes/Shower Policy "OSHA Particularly Hazardous Chemicals" Chemical Management System Perchlorates testing Reproductive and Highly Toxic Chemicals Hydrogen Fluoride Peroxidizable chemicals handling and testing NFPA Target Organ labeling 	
December 2002	Step 4 of the section Using Hazardous Chemicals was revised to add the following requirement: Where the Permissible Exposure Limit (PEL) is exceeded, the person completing the hazard analysis with the concurrence of the PI/Supervisor, will ensure that a written compliance program is developed to reduce employee exposure below the PEL by means of engineering and/or work practice controls.	Worker Safety and Health
April 2002	OSHA-regulated carcinogens (i.e., select carcinogens), reproductive toxins, and substances with a high degree of acute toxicity must be used with engineering controls (hood, glove box, or effective exhaust capturing equipment). Areas must be labeled with "Carcinogen", "Reproductive Hazard", or "Highly Acute Toxin" warning labels or signs. The Carcinogen Sign, Highly Acute Toxin Sign, and Reproductive Toxin Sign were added to this subject area for chemical users to print and nost. See the exhibit on Rules of	Worker Safety and Health

	Laboratory Scale Use of Chemicals.	
October 2001	This subject area describes the guidelines and procedures for working with chemicals at Brookhaven National Laboratory (BNL). It provides information and links to many resources that are designed to aid BNL chemical users, who acquire, manage, use, supervise use, or store chemicals, with essential guidance for chemical safety. It encompasses all components of the BNL Chemical Safety Program, ranging from initial work planning process to disposal. This subject area replaces ES&H Standards 2.1.0, Hazard Communciation Program and 2.1.1, Laboratory Chemical Hygiene Plan.	Worker Safety and Health

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4.1-092004/standard/17/1700a011.htm

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